W71-10651

W71-10651

CLEAN WATER

WATER POLLUTION CONTROL RESEARCH SERIES • 12020 DQC 03/71

PB 201 699

Polymeric Materials for Treatment and Recovery of Petrochemical Wastes

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

ENVIRONMENTAL PROTECTION AGENCY • WATER QUALITY OFFICE

78

POLYMERIC MATERIALS FOR TREATMENT AND RECOVERY OF PETROCHEMICAL WASTES

by

GULF SOUTH RESEARCH INSTITUTE

New Orleans, Louisiana

for the

WATER QUALITY OFFICE
ENVIRONMENTAL PROTECTION AGENCY

Grant No. 12020 DQC

March 1971

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price 70 cents

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Series describes the results and progress in the control and abatement of pollution in our Nation's waters. They provide a central source of information on the research, development, and demonstration activities in the Water Quality Office, Environmental Protection Agency, through inhouse research and grants and contracts with Federal, State, and local agencies, research institutions and industrial organizations.

Inquiries pertaining to Water Pollution Control Research Reports should be directed to the Head, Project Reports System, Office of Research and Development, Water Quality Office, Environmental Protection Agency, Room 1108, Washington, D.C. 20242.

Environmental Protection Agency

Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

1 Accession Number: W71-10651

2 Subject Field & Group: 05D

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

5 Organization
Gulf South Research Institute, New Orleans, Louisiana

6 Title
POLYMERIC MATERIALS FOR TREATMENT AND RECOVERY OF PETROCHEMICAL WASTES

10 Author(s)
Klein, Elias
Desai, Shyamkant V.
Smith, James K.
Weaver, Robert E. C.

16 Project Designation
EPA Program No. 12020DQC 03/71

21 Note
Copy available from GPO Sup Doc, $0.70 in paper, $ copy; microfiche from NTIS as PB 201 699, $0.95.

22 Citation
Water Pollution Control Research Series, March 1971, No. 12020DQC 03/71, 68 pages, 12 fig, 29 tab, 12 ref

23 Descriptors (Starred First)
*Reverse osmosis, *Chemical wastes, Industrial wastes, Separation techniques, *Membranes, Cellulose, Permeability, Viscosity, Pressure, Neutralization, Cost analysis, Evaluation, Amortization, Hydrogen ion concentration, Color, *Waste water treatment, Osmosis, *Oil wastes, Membrane processes,

25 Identifiers (Starred First)
*Glycerin, *Flux, Multi-stage operation, Rejection, Polymeric materials,

27 Abstract
Three operational modes for removing glycerin from waste streams by reverse osmosis were examined. The three modes were: (1) a single-stage reverse osmosis unit which was demonstrated to be capable of removing 27% of the available glycerin, 92% of the inorganics, and 94% of the polyglycerines available in the feed; (2) a three-battery multi-stage unit with forward feed of the raffinate to subsequent reverse osmosis recovery batteries which provided a product stream containing 31% of the available glycerin, no inorganics, and 3.9% of the available polyglycerines; and (3) an alternate two battery multi-stage counter-current recovery unit which provided a waste stream containing 31% of the available glycerin, no inorganics, and 5.2% of the available polyglycerines. Membranes used were asymmetric cellulose acetate butyrate and cellulose acetate. Experimental pilot scale studies performed with tubular membrane models readily accomodated the sample plant stream being used. Optimum selectivity and good separation was achieved under operating pressures ranging from 600 to 800 psig. Product throughput rate appeared to be the limiting factor, being highly sensitive to both increased turbulence and reduced feed viscosities. Analysis of a typical multi-stage forward feed operation operated at 600 psig revealed an estimated capital cost of $133,600 , annual operating expenses of $20,700, and a total yearly credit from a 10 year base depreciation and sale or re-use of the glycerin recovered of $75,610. Payout for the operation was 3.8 years at a 26% rate of return, making it an extremely favorable investment. (Lowry-Texas)

Abstractor: Mark V. Lowry

Institution: Texas Univ, Austin

WR:102 (REV. JULY 1969)
WRSIC

SEND, WITH COPY OF DOCUMENT, TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

(WRSIC abstract)

* GPO: 1970-389-930

ABSTRACT

Reverse osmosis has been used as a unit operation to study the recovery of products from industrial waste streams. Precursory examination of several industrial wastes was performed.

The recovery of glycerin from a petrochemical waste stream containing inorganics and polyglycerins has been studied in detail with the results applied to the design of an effective process scale unit. Membranes employed were asymmetric cellulose acetate butyrate and cellulose acetate. The pilot scale experimental studies were performed with tubular membrane modules which readily accommodated the sample plant stream being studied.

Good separation was achieved operating between 600 and 800 psig for best selectivity. The product throughput rate appeared the limiting consideration and proved sensitive to increased turbulence and reduced feed viscosities ..... the latter achieved by dilution.

The pilot unit data were used to design a countercurrent multistage battery to achieve even closer separations. It is shown that sufficient glycerin could be recovered to provide an attractive return on the required investment.

This report was submitted in fulfillment of EPA Grant No. 12020 DQC from the Water Quality Office, Environmental Protection Agency to the Louisiana Department of Commerce and Industry. The experimental work was performed at Gulf South Research Institute, New Orleans, Louisiana.

CONTENTS

Section		Page
I	Conclusions	1
II	Recommendations	3
III	Introduction	5
IV	Experimental Methods	8
	Apparatus	8
	Process Measurements	12
	Analytical Measurements	12
V	Glycerin Waste Stream	14
	Objectives	15
	Membrane Screening	15
	Process Characterization	22
	Effect of Pressure	22
	Effect of Feed Dilution	32
	Effect of Feed Flow Rate	42
	Effect of Feed Temperature	42
	Multistage Treatment	45
	Projection of Plant Scale Operation	50
	Economic Analysis	57
VI	Propylene Glycol Waste Stream	59
VII	Other Waste Streams	62
VIII	Acknowledgments	64
IX	Bibliography	65
X	Appendix	66

FIGURES

		Page
1	FLAT CELLS UNIT SCHEMATIC	9
2	TUBULAR PILOT UNIT SCHEMATIC	10
3	TUBULAR MODULE SECTION	11
4	FLUX vs. PRESSURE CHARACTERISTIC	23
5	WATER ENRICHMENT	29
6	SEPARATION vs. PRESSURE	30
7	DILUTION vs. PERFORMANCE	40
8	FEED FLOW vs. PERFORMANCE	43
9	TEMPERATURE vs. PERFORMANCE	44
10	SINGLE STAGE OPERATION	51
11	MULTISTAGE FORWARD FEED OPERATION	53
12	MULTISTAGE COUNTERCURRENT OPERATION	55

BLANK PAGE

TABLES

No.		Page
1	GLYCERIN STREAM COMPOSITION	14
2	PHYSICAL PROPERTIES OF THE GLYCERIN STREAM	15
3	MEMBRANE SCREENING FOR GLYCERIN STREAM (Eastman/Amicon Membranes)	17
4	MEMBRANE SCREENING FOR GLYCERIN STREAM (Universal Membranes)	18
5	MEMBRANE SCREENING FOR GLYCERIN STREAM (Tubular Membranes)	19
6	HEAT TREATMENT OF EASTMAN MEMBRANE	20
7	F-P-R CHARACTERISTICS FOR MODULE U-3	24
8	F-P-R CHARACTERISTICS FOR MODULE AS-2	25
9	F-P-R CHARACTERISTICS FOR MODULE U-4	26
10	GLYCERIN REJECTION	27
11	SELECTIVITY INDICES FOR TUBULAR MODULES	31
12	F-P-R DILUTION CHARACTERISTICS - 1	33
13	F-P-R DILUTION CHARACTERISTICS - 2	34
14	F-P-R DILUTION CHARACTERISTICS - 3	35
15	F-P-R DILUTION CHARACTERISTICS - 4	36
16	F-P-R DILUTION CHARACTERISTICS - 5	37
17	F-P-R DILUTION CHARACTERISTICS - 6	38
18	FLUX INCREASE WITH DILUTION	39
19	EFFECTS OF DILUTION ON F-P-R CHARACTERISTICS	41
20	FIRST STAGE RUN (MODULE AS-2)	46
21	SECOND STAGE RUN (MODULE AS-2)	47

TABLES

No.		Page
22	FIRST STAGE RUN (MODULE U-4)	48
23	SECOND STAGE RUN (MODULE U-4)	49
24	MULTISTAGE OPERATIONS	52
25	ECONOMIC ESTIMATION	58
26	DOW WASTE STREAM - 1	60
27	DOW WASTE STREAM - II	61
28	DISPERSE ORGANIC DYE SYSTEM	63
29	REPRODUCIBILITY OF ANALYTICAL RESULTS	68

Section I

CONCLUSIONS

1. The high degree of selectivity necessary for the recovery of many valuable water soluble constituents from concentrated multi-component petrochemical waste streams can be achieved with commercially available reverse osmosis membranes.

2. For the glycerol stream investigated, the membrane throughput (flux) was lower for the undiluted and unfiltered waste streams than for simulated waste streams containing the same components singly. This was due to the higher viscosities of the plant waste, and the limited feed velocity available for the experiments. These factors both lead to increased concentration polarization at the membrane boundary. Both concentration polarization and an indeterminant extent of particulate fouling must be avoided in order to achieve the best possible efficiency.

3. Dilution of the glycerol plant feed stream reduced the severity of concentration polarization and led to marked improvements in production rate. The loss of selectivity as a result of dilution was comparatively insignificant.

4. An experimental module which contained turbulence promoters exhibited a more marked increase in product flux with dilution ratio, than a module without the promoters. The turbulence promoters reduced the boundary layer through mixing.

5. A two-stage separation using diluted feed stock produced product water containing less than 0.3% dissolved solutes. With a proper choice of first and second stage membranes recovery can be made more efficient.

6. Three modes of operation were examined for using reverse osmosis units to recover glycerin, and thereby reduce the waste levels normally sent to the plant waste disposal stream. These three modes are representative only, and are not necessarily the optimum configuration for any plant. They illustrate the recoveries that can be achieved.

   a. A single-stage reverse osmosis unit capable of recovering 27% of the available glycerin can be designed and amortized over 1.5 years based on the current glycerin value. 92% of the inorganics and 94% of the polyglycerines available in the feed, were removed in the product.

   b. A multi-stage recovery unit with forward feed of the raffinate to subsequent reverse osmosis recovery batteries was examined. A three-battery unit provides a product stream which contains 31% of the available glycerin. The product stream contained no inorganics and 3.9% of the available polyglycerines. For some

glycerin purification units the absence of inorganics is necessary. The amortization period for such a design is 3.75 years.

c. An alternative multi-stage recovery unit with countercurrent feed was examined. A two-battery unit provides a product stream which contains 31% of the available glycerin. The design would yield a product containing no inorganics and 5.2% of the available polyglycerines. This is amortized over 4.5 years.

These three designs can be scaled up to recover more glycerin and reduce effluent loadings. Process design calculations may be made based on the objectives established from the examples given.

7. Increased feed temperatures (up to 38°C) increased flux, but with a concurrent reduction in selectivity indices. At temperatures above 38°C, the membrane flux declined.

8. The treatment of glycerin production wastes by reverse osmosis resulted in secondary glycerin recovery. Thus, the effluent loadings are reduced, but the need for final treatment of the raffinates remains.

Section II

RECOMMENDATIONS

This program has confirmed that reverse osmosis membranes do offer the degree of selectivity necessary for the recovery and removal of selected petrochemical waste constituents. To utilize such separation procedures the design engineer must be aware of the interactions between the stream characteristics, the membrane properties, and the flow parameters of the device being used. For separation of solutes in the wastes the selectivity of the membrane must be balanced against the membrane throughput (flux). Improvement of the latter is the most important factor in the design of recovery systems. Because of this need, it is recommended that the following factors be investigated in greater detail:

1. Pretreatment of waste streams to reduce microparticulates which lead to membrane fouling.

2. Practical methods for increasing the degree of turbulence in the tubular modules to reduce concentration polarization.

3. The interactions of several solutes in an aqueous stream to allow better predictions on the rejection of solutes by membranes in such streams.

4. Development of selective membranes which are stable over a wider pH range than the currently available cellulose esters. These could be based on cellulose ethers, which are known to be stable to alkaline hydrolysis.

5. Multi-stage separations designed to utilize more than one type of membrane so chosen to offer both product recovery and water recovery.

6. A simulated field test for the separations detailed here are recommended. The test protocol should be based on a constant feed stream quality, with precautions for pre-filtration. Experimental designs should evaluate the effects of recycle steps, feed dilution followed by recycle, and feed dilution followed by recycle into vacumm distillation units.

7. A number of other petrochemical waste streams having potential for recovery are known to exist; screening experiments with a number of membrane types should be undertaken to evaluate the potential of this process in those areas.

8. The design of various reverse osmosis unit configurations should be examined further to explore the effect of differing design objectives on the processes which can be achieved. For example, the recovery of glycerin of high purity may have different design requirements, than the reduction of chemical oxygen demand in the

effluent. Similarily, the removal of polyglycerin from a solution of glycerin and inorganic salts can be achieved with different process design than either of the two alternatives mentioned. Thus the application of reverse osmosis as a tool in industrial waste disposal requires examination of a number of design objectives and evaluation in terms of both economic return and cost of pollution control.

Section III

INTRODUCTION

This is the final report for the Water Quality Office, Environmental Protection Agency Grant No. 12020 DQC to the Louisiana Department of Commerce & Industry. The research was carried out at Gulf South Research Institute, New Orleans, Louisiana, from June 1969 through June 1970. This report describes the experimental and analytical procedures used in the program and the results obtained therefrom. The objective of this program was to evaluate newly developed semi-permeable membranes for use in in-plant water purification and/or recovery of valuable constituents from petrochemical waste streams.

The need for this study can best be exemplified by describing the water quality problems affecting one section of the Mississippi River which serves as a major water waste collection stream for a petrochemical complex between Baton Rouge and New Orleans, Louisiana. The river serves as the outfall collector for a refining capacity well in excess of 600,000 barrels of oil per day. In addition, a varied and large chemical industry is based on these refined products, and adds to the effluent loadings.

Current levels of organic extractables are between 0.5 and 1.0 ppm. These levels are above the recommended maximum (0.25 ppm). The average C.O.D. in the river is 50 ppm. Of this amount, 15 to 20 ppm have been attributed to petrochemical sources. With a flow of 400,000 ft^3/sec., this represents 100,000 tons/day of petrochemicals. At an average price of six cents per pound, this amounts to a loss of $150,000/day in material. The recovery of useful chemicals is therefore not only an ecological problem, but has economic incentives as well.

An equally important incentive is the development of in-plant water purification for recycle purposes. The estimation (1) that by the year 2000 this nation may face a 200-400 billion gallons per day deficit of economically extractable fresh water gives a clearer idea of the magnitude of the problem. In this connection, it should be pointed out that in an optimally designed reverse osmosis system, the recovery of constituents and the production of potable water go hand-in-hand.

Basically, osmosis is the flow of a solvent from a solution of higher solvent concentration to a solution of lower solvent con-

centration across a semi-permeable membrane. The driving force for solvent flow is the osmotic pressure difference which is proportional to the difference in solute concentration between the two solutions. If external pressure in excess of the osmotic pressure difference is applied, a reversal of solvent flow occurs, hence the term "reverse osmosis". By these means, water, containing impurities, can be forced through a suitable membrane, leaving the impurities behind in concentrated solution.

The dual objective of product recovery and water purification was pursued by:

i) A membrane screening program to establish the waste streams and membranes suitable for trial, and

ii) Characterization of selected systems to derive engineering design criteria. Membrane screening was undertaken to evaluate the various types of commercially available membranes for their ability to separate some prototype solutes. These were based initially on a disperse dye (Cibacete) as representative of large solutes with limited solubility; on glycerin as representative of a water soluble solute of intermediate molecular weight; and on NaCl as representative of the ionic low molecular weight solutes. The relative rejection ratios of these solutes, together with the hydraulic permeability of the membranes were used as a preliminary characterization.

Following the screening program, a more detailed study of the separation and throughput characteristics of specific systems was undertaken. The operating ranges of pressure, feed concentration, feed flow rate, and temperature were evaluated. These data are necessary for subsequent engineering design calculations to be made.

Unfortunately, present understanding of the transport processes through membranes is not adequate to predict the behavior of multicomponent systems, even when the transport of the components singly is known. Agrawal and Sourirajan (2) have suggested a method for the prediction of membrane performance with multicomponent aqueous feeds based on a generalized diffusion model (3). The method is said to be applicable only to multicomponent feeds having a common ion. However, the solutions under study here do not meet this requirement, so that completely phenomenological data must be gathered, although a number of experiments were carried out on the single components for future reference in a parallel study (4).

Through the cooperation of Shell Chemical Corporation, we have studied in detail one aqueous waste stream containing glycerin, inorganic salts, and other organic solutes. The separation sought

would allow separation of the glycerin (product) from the other organic and the inorganic solutes, in such a manner that it would be suitable for glycerol manufacturing process, (4). A related stream from Dow Chemical Company was also studied, but with less success.

In addition to the two pilot streams, a simulated process stream containing disperse dye was evaluated during the initial stages of this project. The dye was found to be very tractable by this purification method. Both high recoveries of the expensive dye and good quality water were obtained with prototype streams, but further study on this stream could not be undertaken for a lack of participating interest.

Section IV

EXPERIMENTAL METHODS

APPARATUS.

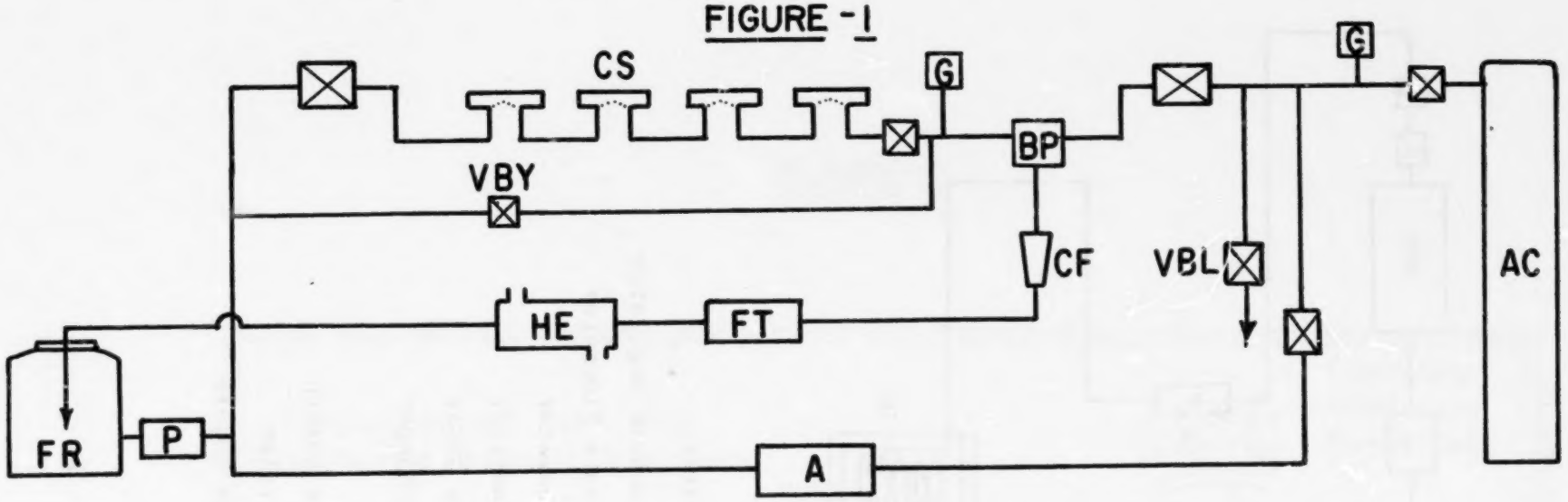
Two types of reverse osmosis circuits were used in this research. A small cell test circuit using flat sheet membranes was employed for screening of membranes to establish their separation efficiencies and product rates. Once membrane types and stream details had been selected, the studies were scaled up to a larger reverse osmosis circuit using tubular membranes arranged into packaged modules of four tubes each.

1. Flat Cell Reverse Osmosis Unit. This unit was used for initial evaluations of flat membranes at pressures up to 1500 psi. It consists of a Milton Roy duplex pump with a capacity of 24 gph at 1500 psig, pumping through a Nupro 10 micron in-line filter. The test cells are built according to a General Atomics design, and use a rectangular flow pattern. Between the filter and the three test cells, a T-joint connects a Greer 10 cu. in. accumulator pressurized with nitrogen. The line is maintained at constant pressure with a Model 8-91 Mighty Mite back pressure regulator. A Brooks flowmeter is in the low pressure return line following the pressure regulator. The effluent returns to the feed reservoir via a tap water cooled heat exchanger. By maintaining the temperature of the return fluid it is possible to maintain the temperature differential across the circuit at a constant value. Fig. 1 shows the schematic of the flat plate cell circuit.

2. Tubular Reverse Osmosis Unit. The flow diagram of this unit is shown in Fig. 2. It was designed and sold by American Standard Co. and is scaled to be suitable for pilot evaluations. The distinguishing feature of this unit is the tubular design of the membrane module. It consists of four porous 1/2" diameter, 27" long fiberglass reinforced epoxy tubes which in operation are lined with the membranes to be tested. This unit can be adapted to larger tubular modules from all suppliers and could possibly be employed with any membrane module unit.

Solution is circulated through the module and recycled to the feed tank. A Yarway diaphragm pump capable of delivering 51.5 gph at 2000 psi was used. Both input and return flows are monitored by flowmeters; flow pulsations are damped by two accumulators, one on the inlet and another on the outlet side of the module. The membrane permeate (or product) goes into the

FIGURE - 1

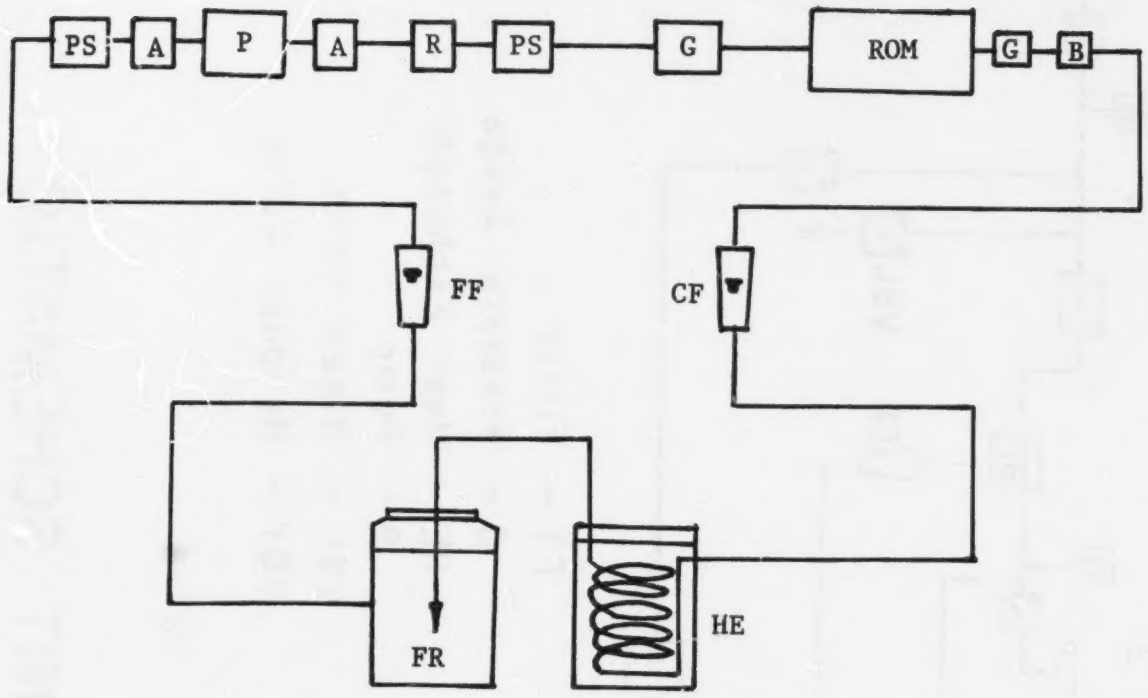


A - Accumulator
AC - Air Cylinder
BP - Back Pressure Regulator
CF - Concentrate Flowmeter
CS - Flat Cell Bank
FR - Feed Reservoir
FT - Filter
G - Pressure Guage
HE - Heat Exchanger
P - Pump
VBL - Bleed Valve
VBY - By-pass Valve

⊠ - Needle Valve

FLAT CELLS UNIT SCHEMATIC

TUBULAR PILOT UNIT SCHEMATIC



A - Accumulator

B - Back Pressure Regulator

CF - Concentrate Flowmeter

FF - Feed Flowmeter

FR - Feed Reservoir

G - Pressure Gauge

HE - Heat Exchanger

P - Pump

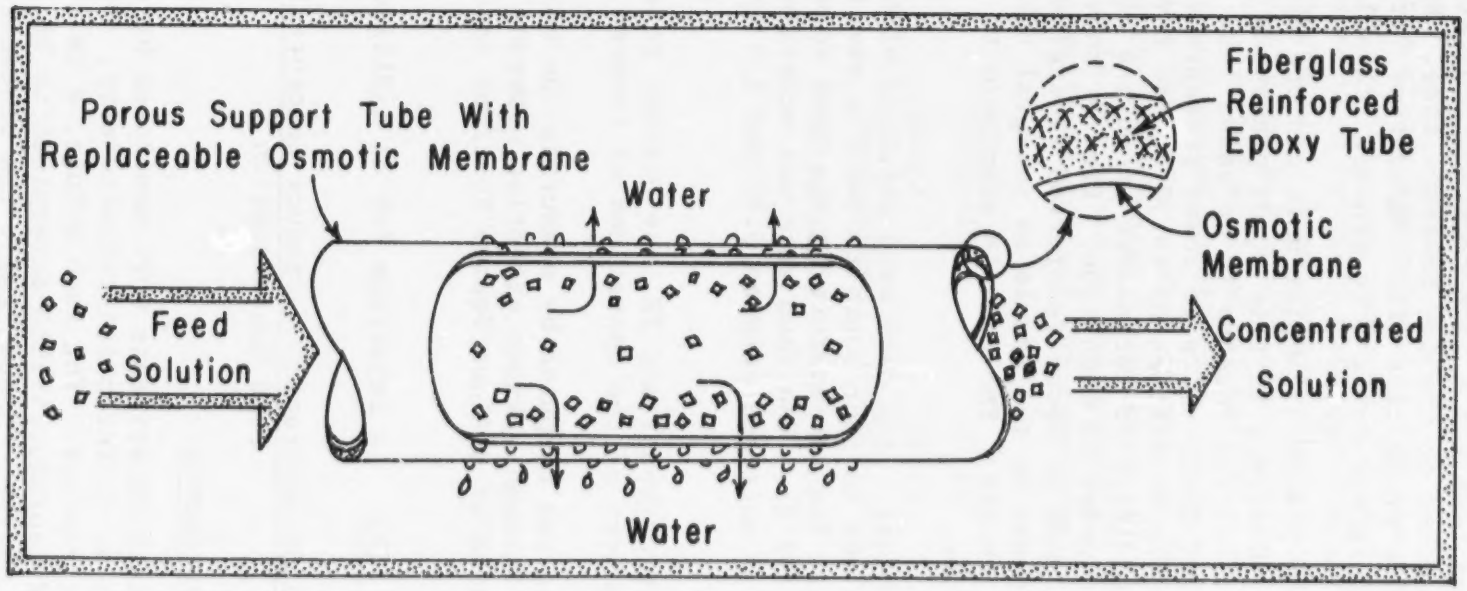
PS - Pressure Switch

R - Safety Valve

ROM - Membrane Module

Figure - 2

FIGURE -3



TUBULAR MODULE SECTION

collection shroud, and the concentrated feed inside the tubes returns to the feed tank via a back-pressure regulator. The return is metered and cooled on the low pressure side. Because of the change in membrane properties with temperature, it is necessary to control the temperature to ±2°C to produce reliable data.

The American Standard tubular unit can operate at pressures up to 2000 psi. However, in this study pressures of 1200 psi and lower were used, for reasons to be shown later. Some module suppliers do limit their units to lower pressure with 1/2" i.d. tubes. With linear velocities up to 50 cm/sec turbulent flow should occur. Addition of turbulence promoters will increase turbulence by an order of magnitude. Fig. 3 shows the tubular membrane module made of epoxy reinforced fiberglass tubes. Membranes are loaded in the module as integral tubes or as formed units from flat sheets. The unit is adaptable to various sizes of tubular modules.

Process Measurements. All data were obtained with experiments lasting between two to four hours to reach a steady state before taking a sample. The temperature of the feed solution was maintained at 25°C (±2°C). The feed rate was maintained at 0.4 gpm on the flat cells unit and between 0.85 and 1.0 gpm on the tubular unit.

Flux (or throughput) and %R, the percent rejection, are the two major parameters of the operations of reverse osmosis.

Flux: This was computed by measuring the volume of a permeated product through a known effective membrane area per unit time and expressed as Gallons/Square Foot/Day (gfd) at a fixed pressure.

Rejection (%R): A rejection for an individual constituent is defined as:

$$\%R = \frac{\text{Feed Concentration - Product Concentration}}{\text{Feed Concentration}} \times 100$$

Analytical Measurements:

Single solute experiments were monitored by classical analytical techniques such as differential refractometry, conductivity and absorbence spectroscopy. For each solute, a calibration curve was constructed and reproducibility determined to be at least a tenth of one percent or better. Specifically the concentrations of glycerin and polyglycols were followed with differential refractometry,

sodium chloride concentration was monitored by changes in conductivity and dye content was followed using spectrophotometric techniques.

Multi-component analysis was necessary for the process waste stream and required a specific approach. The method employed followed the suggested procedure used by Shell Chemical Company in their quality control laboratories. Summarizing, the glycerin content was determined by a titration method specific for glycerin, the water component was monitored using a classical Karl Fisher titration or by weight loss under controlled conditions, the inorganics were determined by weighing the residue upon ashing and the polyglycerines were determined from the differences in weight. The detailed procedure for the analysis is described in the appendix. The deviation of the analysis between multiple test of the same sample is estimated to be:

Glycerin	±0.1%
Water	±0.5%
Inorganics	±0.1%
Polyglycols	±0.8%

Section V

GLYCERIN WASTE STREAM

A waste stream from the glycerin manufacturing plant of Shell Chemical Company, Norco, Louisiana, was studied for possible recovery of glycerin. The aqueous stream contains glycerin, various polyglycerines (molecular weight > 100) and a mixture of inorganics (presumably sodium chloride and sodium hydroxide). A detailed review on processes for manufacture of glycerin is made by N. Shreeve (5). At present this stream is wasted since the inorganics and the organics cause fouling of heat exchangers, corrosion of the equipment, foaming in boilers and cooling towers and affect the efficiency of the stripping operation. It was, therefore, necessary to reduce these constituents to a minimum in order to obtain a usable recycle stream.

The waste stream composition is listed in Table 1. The two samples, obtained at two different times from the plant vary in composition, especially with respect to glycerin content.

TABLE - 1

GLYCERIN

STREAM COMPOSITION

Constituent	Sample No. 1 % Wt.	Sample No. 2 % Wt.
Glycerin	1.2	2.7
Polyglycerines (Molecular Weight >100)	14.2	17.3
Sodium Chloride + Sodium Hydroxide	2.7	3.0
Water	81.9	77.0

The variation may be due to the process upsets or changes in operating conditions. The stream also contained some suspended matter.

The physical properties of the stream are listed in Table 2. It is believed that the osmotic pressure of the stream is mainly due to glycerin and the inorganics, whereas, the viscosity is due to the polyglycerines present at a relatively higher concentration. It was necessary to adjust the pH of the waste stream to 7 with phosphoric acid in order to preserve membrane life.

TABLE - 2

PHYSICAL PROPERTIES OF THE GLYCERIN STREAM

Color	-	Dark Brown
Odor	-	None
Density gms/cm^3	-	1.05
Viscosity (Centipoises)	-	1.5
pH	-	8 - 9
Suspended Matter	-	Removable by 10 micron filter

Objectives:

The specific objectives to be met in formulating a solution were:

i) To identify one or more commercially available membranes that will selectively retain inorganics and polyglycerines letting glycerin and water pass through at an optimum flux.

ii) Having chosen such membrane(s), to completely characterize the membrane-waste stream system under single stage and multistage operating conditions.

iii) Based on the data obtained, to project a feasible process scale recovery system and to make a primary economic evaluation of such a system.

Membrane Screening:

Three types of commercial membranes were screened for the present application;they were:

i) Asymmetric Cellulose acetate-butyrate membranes (supplied by Universal Water Corp.)

ii) Loeb type desalination membranes made from secondary cellulose acetate (supplied by Eastman Organic Chemicals and American Standard)

iii) Polyelectrolyte Complex Membranes (supplied by Amicon Co.)

The first two types of membranes are representative of the developments resulting from a large program directed toward recovering potable water from sea water and brackish water. The details of the manufacture, structure, and mode of action of such membranes have been reviewed in a number of Department of Interior publications available through the U.S. Government printing office. Because of the great interest in the application of such membranes to desalination and the resulting growing literature, it is not necessary to review their properties here. The polyelectrolyte membranes have been described in a number of publications available through the manufacturer. Since much of the details of manufacture are proprietary, no review can be provided.

Sodium Chloride, Glycerol, Polyethylene Glycol (Molecular Weight 380-420), Polyethylene Glycol (Molecular Weight 580-620) and Cibacete Dye were used as representative solutes; the salt represented inorganics, and Polyethylene Glycols represented other organics. These choices represented severe test solutes. The throughput (flux) and separation characteristics of these solutes at 10,000 ppm concentration, at 600/800 psig applied pressure and 0.4 gpm flow rate were obtained. Primarily, the flat cells unit was used for this purpose, however, the tubular unit was also used when testing membrane modules.

Tables 3 and 4 illustrate the data obtained on the flat plate cell test circuit with asymmetric cellulose derivatives and Amicon membranes. Table 5 lists the data obtained on tubular module test circuit. These data can be used to point out some general properties of asymmetric membranes to those readers not familiar with their characteristics. Increased rejection of sodium chloride is generally coupled with reduced flows. The reduced flow is a result of two factors; first, it has been extremely difficult to prepare membranes which exhibit high fluxes, and at the same time are "tight"; i.e., prevent NaCl from permeating. Secondly, if a membrane is in fact "tight" to the solute in question, the resulting semipermeability (i.e. water permeability, but solute impermeability) results in the creation of an osmotic pressure, which acts in opposition to the applied hydrodynamic pressure. To separate the two effects, it is a general practice to measure water permeability (usually referred to as hydraulic permeability) in the absence of any solutes. The decreased water flux found subsequent to the addition of solute to the test solution can then be compared to the theoretically calculatable osmotic pressure. If in fact there is a larger decrease than can be accounted for by the creation of the osmotic pressure, the decrease is often a result of compression of the membrane or fouling by high molecular weight materials.

TABLE - 3

MEMBRANE SCREENING FOR GLYCERIN STREAM

EASTMAN/AMICON MEMBRANES

Eastman Membrane

Solute Concentration: 10,000 ppm Pressure: 800 psi Geometry: Flat Cell

Membrane No.	NaCl Flux gfd	NaCl Reject %	Glycerin Flux gfd	Glycerin Reject %	Polyol 400 Flux gfd	Polyol 400 Reject %	Polyol 600 Flux gfd	Polyol 600 Reject %
RO-89	27.9	88.0	26.2	79.7	26.0	95.0	-	-
G-2	3.4	99.6	3.0	96.6	6.3	96.5	-	-
G-3	4.6	99.6	4.9	95.0	5.4	97.4	-	-
G-4	41.5	0.77	33.7	9.6	43.3	31.0	35.2	36.8
G-5	47.0	29.0	35.7	32.8	68.9	61.7	49.5	63.2
G-6	39.8	42.4	48.3	34.3	33.6	69.0	45.2	76.5
G-7	34.7	53.7	38.7	59.0	32.6	88.0	38.2	92.0

Amicon Membrane

Pressure: 70 psi

(Other test conditions same as above)

UM-05	6.29	0	6.15	11.9	5.64	88.2	6.85	91.3

TABLE - 4

MEMBRANE SCREENING FOR GLYCERIN STREAM UNIVERSAL WATER CORPORATION MEMBRANES

Solute Concentration: 10,000 ppm Geometry: Flat Cell

Membrane No.		NaCl		Glycerin		Polyol 400		Polyol 600	
		Flux gfd	Reject %	Flux gfd	Reject %	Flux gfd	Reject %	Flux gfd	Reject %
CAB-171-15	(a)	5.7	93.7	6.2	> 99.0	5.8	> 99.0	6.3	> 99
	(b)	7.4	98.3	8.4	> 99.0	8.4	> 99.0	8.4	> 99
CAB-171-25	(a)	6.0	96.0	6.1	98.2	6.7	> 99.0	6.9	> 99
	(b)	7.9	97.2	8.0	99.0	8.7	> 99.0	9.2	> 99
IV-64-2	(a)	198.4	1.2	81.5	0.9	61.3	4.8	39.6	4.3
	(b)	212.0	3.6	62.0	5.9	70.1	5.9	49.9	4.8
IV-64-2 (76°)	(a)	58.0	67.0	64.6	52.2	51.5	83.0	43.6	91
	(b)	76.6	69.0	80.3	55.4	66.3	84.0	56.0	98
IV-64-2 (81°)	(a)	30.0	91.0	34.6	87.6	36.6	96.2	35.6	> 99
	(b)	44.9	93.0	47.2	89.2	49.4	94.0	45.2	> 99
IV-64-3	(a)	60.0	13.8	53.1	5.7	45.3	17.5	54.1	18.1
	(b)	78.1	18.7	53.7	8.8	57.1	34.8	68.5	18.8
IV-64-3 (76°)	(a)	55.0	67.0	54.5	60.2	58.9	80.2	46.3	92.1
	(b)	72.2	73.9	67.6	63.7	69.5	81.8	56.6	92.7
IV-64-3 (81°)	(a)	20.2	83.2	22.4	85.2	25.6	91.8	20.7	96.2
	(b)	23.0	89.5	29.7	84.1	33.4	92.5	27.5	97.2
IV-64-4	(a)	62.8	9.6	42.6	3.8	46.3	17.8	32.0	29.4
	(b)	69.7	16.7	47.7	10.5	50.1	18.0	39.3	29.5
IV-64-4 (76°)	(a)	50.1	76.4	51.1	50.2	44.1	82.9	40.9	87.6
	(b)	68.8	77.0	64.4	50.5	51.1	84.6	58.4	90.8
IV-64-4 (81°)	(a)	15.9	90.6	17.6	85.6	18.3	96.8	19.1	> 99
	(b)	22.5	91.1	25.3	86.4	28.3	98.5	26.8	> 99
IV-64-5	(a)	53.0	12.0	39.8	6.0	32.4	17.4	31.8	21.4
	(b)	63.1	15.7	48.3	6.6	40.1	22.3	42.8	25.8
IV-64-5 (76°)	(a)	54.2	59.3	51.8	55.6	51.9	85.2	41.8	90.8
	(b)	72.2	62.4	70.1	60.4	61.4	87.9	49.4	93.7
IV-64-5 (81°)	(a)	18.8	90.1	21.4	83.1	21.0	98.7	21.5	> 99.0
	(b)	26.2	90.8	27.0	84.1	30.4	> 99.0	27.0	> 99.0

(a) = Operating Pressure 600 psig (b) = Operating Pressure 800 psig

TABLE - 5

MEMBRANE SCREENING FOR GLYCERIN STREAM TUBULAR MEMBRANES

Solute Concentration: 10,000 ppm

Feed Flow Rate: 0.9 gpm

Membrane No.	Pressure psig	NaCl Flux gfd	NaCl Reject %	Glycerin Flux gfd	Glycerin Reject %	Polyol 400 Flux gfd	Polyol 400 Reject %	Polyol 600 Flux gfd	Polyol 600 Reject %
Amer. Std.									
AS-1 CellAcet	600	18.9	91.2	13.8	92.1	16.3	98.1	15.9	98.2
	800	22.3	93.5	19.9	93.0	22.3	98.4	21.7	99.1
AS-2	800	61.2	73.0	48.3	75.5	55.0	94.9	50.7	96.0
Eastman									
G-5	800	29.4	10.5	25.0	10.0	23.7	38.0	22.0	41.2
Universal Water									
U-1 CAB	600	24.7	83.5	27.0	72.3	25.7	89.3	25.6	91.4
	800	33.0	85.6	36.4	75.5	34.1	93.2	34.1	93.2
U-2 CAB	800	38.8	74.0	37.1	68.4	38.5	92.5	37.2	95.0
U-3 CAB	800	46.7	64.2	47.2	60.1	44.6	81.6	48.4	85.9

CellAcet - Cellulose Acetate

CAB - Cellulose Acetate Butyrate

A second general phenomenon to be observed is that as the pressure is increased, the water flux increases, but the solute flux does not increase. Since the rejection ratio is a function of the ratio of solute and solvent fluxes, the rejection ratio increases with pressure. The absence of solute flux response to pressure is the basis for desalination by reverse osmosis, since increased pressure thus leads to greater productivity, and purer water. But for separations of multisolute streams, it can be a disadvantage, as will be shown later. In the case of mixed solutes, it is true that increased pressure leads to higher fluxes, and also to higher rejection ratios, but it lowers separation efficiencies since all of the solutes are rejected more effectively.

The third significant phenomenon illustrated in these tables is the effect of heat treatment on the thermoplastic membranes. The procedure for preparing membranes from cellulose esters consists of quenching a multicomponent gel in an aqueous solution. The membrane at that stage has very high permeability, and only moderate rejection properties (See IV-64-2 in Table 4). The membranes then undergo a structural change by being subjected to an aqueous heat treatment which results in a marked decrease of permeability, an increase in rejection ratio, and a moderate stabilization against further flux losses (See IV-64-2 [81] in Table 4). Since the degree of rejection of the various solutes is not affected identically, this preparation variable offers a technique by which separation efficiency can be manipulated. The details of the heat treatments employed for Eastman membranes listed in Table 3 are given in Table 6.

TABLE - 6

Membrane No.	G-2	G-3	G-4	G-5	G-6	G-7
Shrinkage Temp. °C	83	83	-	83	75	75
Time, Seconds	90	120	-	17	240	300

Selections were made for further screening in the tubular unit based on the flat plate tests. While the membranes that were to be used in the tubular tests were available in sheet form, the design of the American Standard module allowed them to be loaded. This was accomplished by the use of narrow membrane strips which were glued around a withdrawable mandrel to form tubular elements. The purpose of these trials was to establish if the improved boundary layer properties of the larger unit were reflected in improved performance. Unfortunately, the vagaries of reproducing the glue line, heat treatment, and "shadowing" of an indeterminate area of the membranes precluded a rigorous answer.

Instead of continuing with further trials to load sheet membranes into a tubular unit, a decision was made to obtain the best tubular castings available to the project. The results of the flat sheet trials were used as specifications to membrane suppliers to guide their preparations. From the results of the experiments available, it was concluded that the samples:

IV-64-2 (76°)
IV-64-3 (76°)
IV-64-4 (76°)
G-5
G-6
G-7
UM-05

merited further investigation.

The IV-64 series showed similar properties, and were all representative of mild heat treatment. Consequently, Universal Water Corp. was asked to supply a 7.01 sq ft. tubular membrane module with the properties similar to the IV-64 series noted above. Upon receipt this was designated U-1; its properties are shown in Table 5. It is apparent that the flux and rejection properties are different from the sheet membranes used for specification. The tubular unit has approximately 50% lower flux, but a compensatory rise in rejection. Since this increased rejection was found to be true for all solutes tested individually, there was a loss of separation. This consideration overrode all other factors, and the unit was returned for another casting. As a result Universal Water Corporation resubmitted two units, designated U-2 and U-3, whose properties are also shown in Table 5. While the separation factors were still not as good as the sheet submissions, it was decided that the trials should proceed with U-3 to characterize the actual plant streams. During initial testing with the waste stream membrane failure occurred in module U-3. Module U-4 (a replacement for U-3) was, therefore, procured from Universal Water Corporation. U-4 was tested at pressures not exceeding 800 psig.

Two submissions from American Standard comprising 1.04 sq. ft. tubular units were also chosen for evaluation on the plant streams. These units (AS-1 and AS-2) were cast directly on to the tubular support; in addition, they contained turbulence promoters, in the form of 7/16" diameter PVC balls. Table 5 indicates that AS-2 had a higher flux and a better separation potential than AS-1, although the latter is more highly rejecting.

The literature provided by the manufacturer of Dialfo membranes indicated that a good separation of glycerin could be obtained from the higher polyols. The salt rejection would, however, be essentially zero, so that the glycerin and salt would permeate together with the water. For the specific purpose contemplated, i.e., refeed to the glycerin distillation unit, this separation was not advantageous. The unfavorable separation, coupled with the limited range of pressures over which they could be used, suggested that further work on these membranes should be deferred.

As a result, the screening experiments yielded two modules which were then used for process characterization. These were the AS-2 and U-4 units.

Process Characterization:

The membranes selected in the screening were subjected to a detailed study of their performance with the glycerin waste stream as a feed. The study involved effect of change of:

i) Pressure (range: 500 psig - 1200 psig),

ii) Feed concentration (range: 0 to 50% dilution),

iii) Feed velocity (range: 0.5 to 1 gpm), and

iv) Temperature (range: 20°C to 70°C)

on the flux and rejection characteristics of the membrane. This was termed as "process characterization" because of its potential importance in the process design of reverse osmosis systems.

Effect of Pressure on the Membrane Performance:

Tables 7 - 9 inclusive list the Flux-Pressure-Rejection (FPR) characteristics of modules U-3, AS-2 and U-4 respectively. While the specified maximum operating pressure for AS-2 was listed as 1500 psi we limited the trials to 1200 psi in view of the unfortunate experience with the U-3 module.

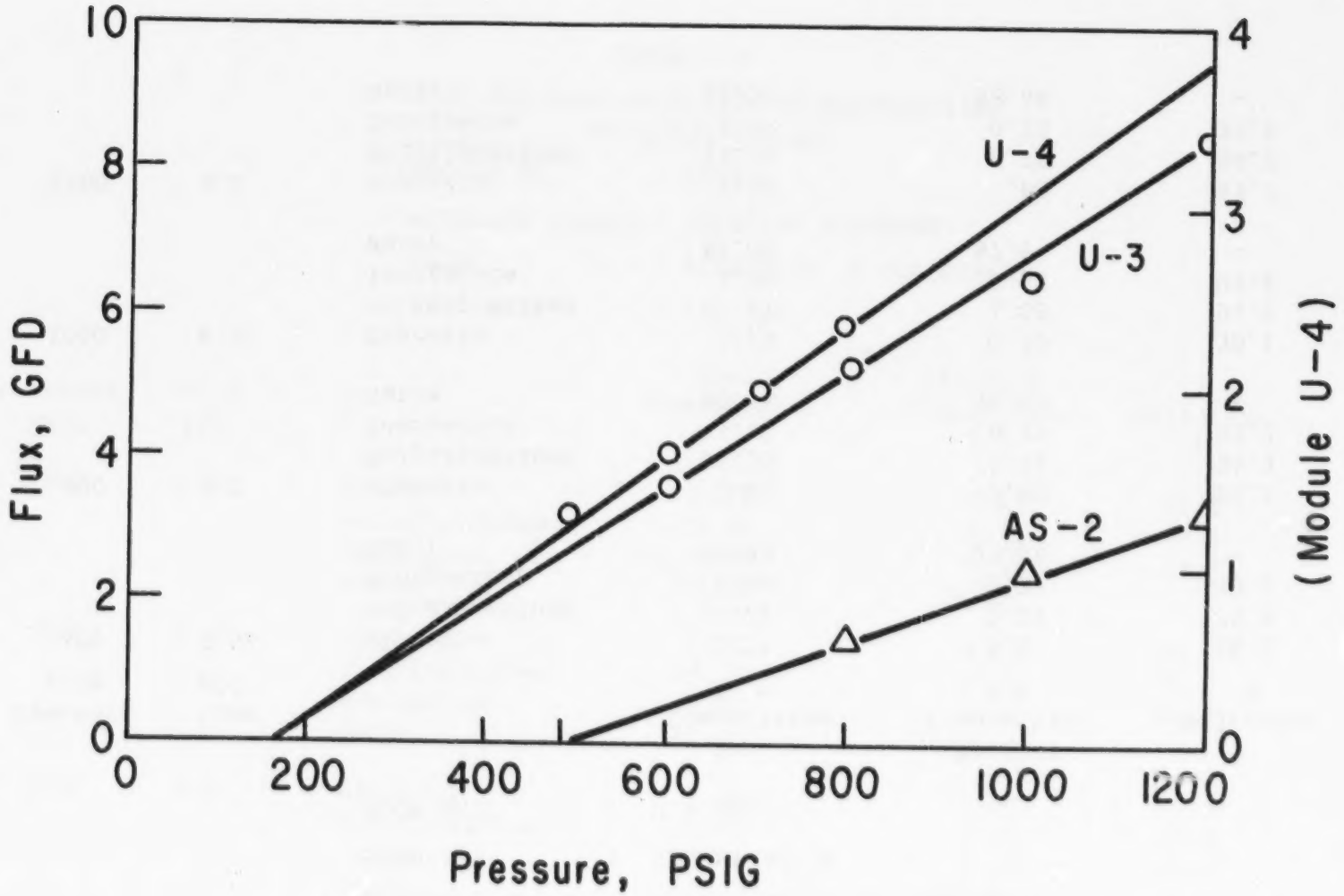
Study of the three tables reveals that some general phenomena can be deduced. The water flux increases almost linearly with pressure; the rejection of organics and inorganics increase almost linearly with pressure; the flux decreases markedly from the flux observed with single component experiments; and the absolute values of the rejections are altered significantly in the mixture from comparable values tested singly.

These generalizations can best be illustrated graphically. In Figure 4 are shown the flux values for units AS-2, U-3 and U-4 as a function of pressure. Three observations are significant in this graph. As mentioned earlier there is a linear relationship between the flux and the pressure, so that an algebraic function can be derived readily; the slope of the line is a measure of the hydraulic permeability of the membranes forming the module; from the data one can deduce that the AS-2 membrane is the "tighter" of the three.

The slope of the line is compatible with the description of flux given by

$$J_w = L_p (\Delta P - \Delta\pi) \qquad (1)$$

where J_w is the flux, L_p the hydraulic permeability, P the applied pressure gradient, and $\Delta\pi$ is related to the concentrations and reflection coefficients of the membrane by



FLUX vs PRESSURE CHARACTERISTIC

FIGURE - 4

TABLE - 7

FLUX-PRESSURE-REJECTION CHARACTERISTICS
(Original Stream)

MODULE NO. : U-3

MEMBRANE SOURCE : UNIVERSAL WATER CORPORATION

FEED : STREAM NO. 8

FLOW RATE : 0.9 gpm

No.	Pressure psig	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	600	3.58	Glycerin	1.19	1.0	16.1
			Polyglycerines	14.22	3.28	76.8
			Inorganics	2.66	0.32	88.0
			Water	81.93	95.48	-
2	800	5.2	Glycerin	1.03	0.80	22.3
			Polyglycerines	15.33	2.41	84.3
			Inorganics	3.10	0.15	95.2
			Water	80.54	96.64	-
3	1000	6.45	Glycerin	1.13	0.70	38.1
			Polyglycerines	13.11	1.08	91.8
			Inorganics	3.76	0.33	91.2
			Water	82.00	97.9	-
4	1200	8.4	Glycerin	1.16	.63	45.7
			Polyglycerines	13.72	0.73	94.7
			Inorganics	3.57	0.23	93.6
			Water	81.55	98.44	-

TABLE - 8

FLUX-PRESSURE-REJECTION CHARACTERISTICS
(Original Stream)

MODULE NO. : AS-2

MEMBRANE SOURCE : AMERICAN STANDARD

FEED : STREAM NO. 8 (ORIGINAL)

FLOW RATE : 0.9 gpm

No.	Pressure psig	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	800	1.43	Glycerin	1.57	0.69	56.1
			Polyglycerines	13.02	1.35	89.6
			Inorganics	2.79	0.35	87.5
			Water	82.62	97.61	-
2	1000	2.49	Glycerin	1.54	0.55	64.3
			Polyglycerines	12.69	0.67	94.7
			Inorganics	2.84	0.27	90.5
			Water	82.63	98.51	-
3	1200	3.21	Glycerin	1.57	0.45	71.3
			Polyglycerines	13.07	0.53	95.9
			Inorganics	2.89	0.18	93.8
			Water	82.47	98.84	-

TABLE - 9

FLUX-PRESSURE-REJECTION CHARACTERISTICS

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

FEED : STREAM NO. 8 (ORIGINAL)

FLOW RATE : 1.0 gpm

No.	Pressure psig	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	500	1.55	Glycerin	2.70	2.70	-
			Polyglycerines	17.42	9.93	43.0
			Inorganics	2.99	1.64	45.2
			Water	76.89	85.73	-
2	600	1.61	Glycerin	2.72	2.65	2.6
			Polyglycerines	17.64	7.45	57.8
			Inorganics	3.04	1.09	64.2
			Water	76.60	88.81	-
3	700	1.98	Glycerin	2.65	2.65	-
			Polyglycerines	17.71	6.85	61.3
			Inorganics	2.96	0.99	66.6
			Water	76.68	89.51	-
4	800	2.35	Glycerin	2.72	2.46	9.6
			Polyglycerines	17.93	6.88	61.6
			Inorganics	3.11	1.04	67.0
			Water	76.24	89.62	-

$$\Delta\pi \propto \Sigma\sigma_i \cdot C_i \qquad (2)$$

The net driving force is a function of the feed concentration, applied pressure, and the rejection coefficients for the solutes being separated. Referring again to Figure 4, the slope of AS-2 is lower than the corresponding slopes for U-3 and U-4 indicating that the former has lower intrinsic permeability. The lower permeability is often accompanied by a "tighter" structure, as indicated by the higher rejection ratios found with single solute tests (See Table 5). It is also confirmed by the effective osmotic pressure found by setting J_w equal to zero in equation (1). For U-3 and U-4 the back osmotic pressure at the point that $J_w = 0$ is found to be 160 psi; for AS-2 the same intercept is found at 475 psi.

From equation (2) it is apparent that it is the sum of the $\sigma_i \cdot \Delta c_i$ products which contribute to the back pressure. Since the several solutes are present in varying molar concentrations, and exhibit different reflection coefficients (σ_i), it is not an easy task to assign the relative sources of osmotic back pressure to the solutes. The situation is further complicated by the non-ideality of the system; i.e., in eqn (2) above it is assumed that no interaction exists between the solutes resulting in zero values for the cross coefficients. The mechanical formation of boundary layers whose concentrations differ significantly from the bulk concentrations, also confounds the assignment of the osmotic pressure to the individual solutes. Consequently, one can only use very general guides at this point in directing membrane development work toward improved separations until such time as the interactions of the various physical chemical parameters can be isolated.

A direct comparison of some of the factors itemized above is possible in the case of glycerin separations. By retabulating the rejection of this solute from the data when it is a single solute and when it is present in a mixture of solutes, the comparisons can be drawn:

TABLE - 10

GLYCERIN REJECTION (%) AT 800 psi

U-3		AS-2	
Single	Mixture	Single	Mixture
60.1	22.2	75.5	55.9

The characterization of membrane performance for separation of multi-component streams requires that several indices must be developed. The efficacy of the separation can be examined from the point of alternative which might be accomplished; this is the most pragmatic way of describing performance, and we shall utilize it in the sections

to follow. For example, the product stream resulting from U-3 is richer in water than the feed; the extent of this enrichment as a function of pressure is shown in Figure 5, but the increase from 82 to 98% is not a very sensitive index.

Figure 6 shows the relationship between recovery/rejection and applied pressure. It is seen that polyglycerines and inorganics rejection increased with the pressure thus providing a purer product, but the higher pressure was not advantageous for the glycerin recovery since the glycerin recovered in the permeate decreased from 83.9% at 600 psig to 54.4% at 1200 psig.

The three curves in Figure 6 thus summarize the potential of separation; both inorganic and organic levels in the permeate can be reduced substantially, while only a relatively minor percentage of the glycerin level is reduced. The permeate thus may be suitable for reprocessing in the original recovery unit since the deleterious components - inorganics and higher molecular weight polyols - have been reduced substantially.

An algebraic index of this type can also be developed in the following manner if a selectivity index for organics is defined:

$$S_o = (\%\ \text{Rejection of Organics} - \%\ \text{Rejection of Glycerin})$$

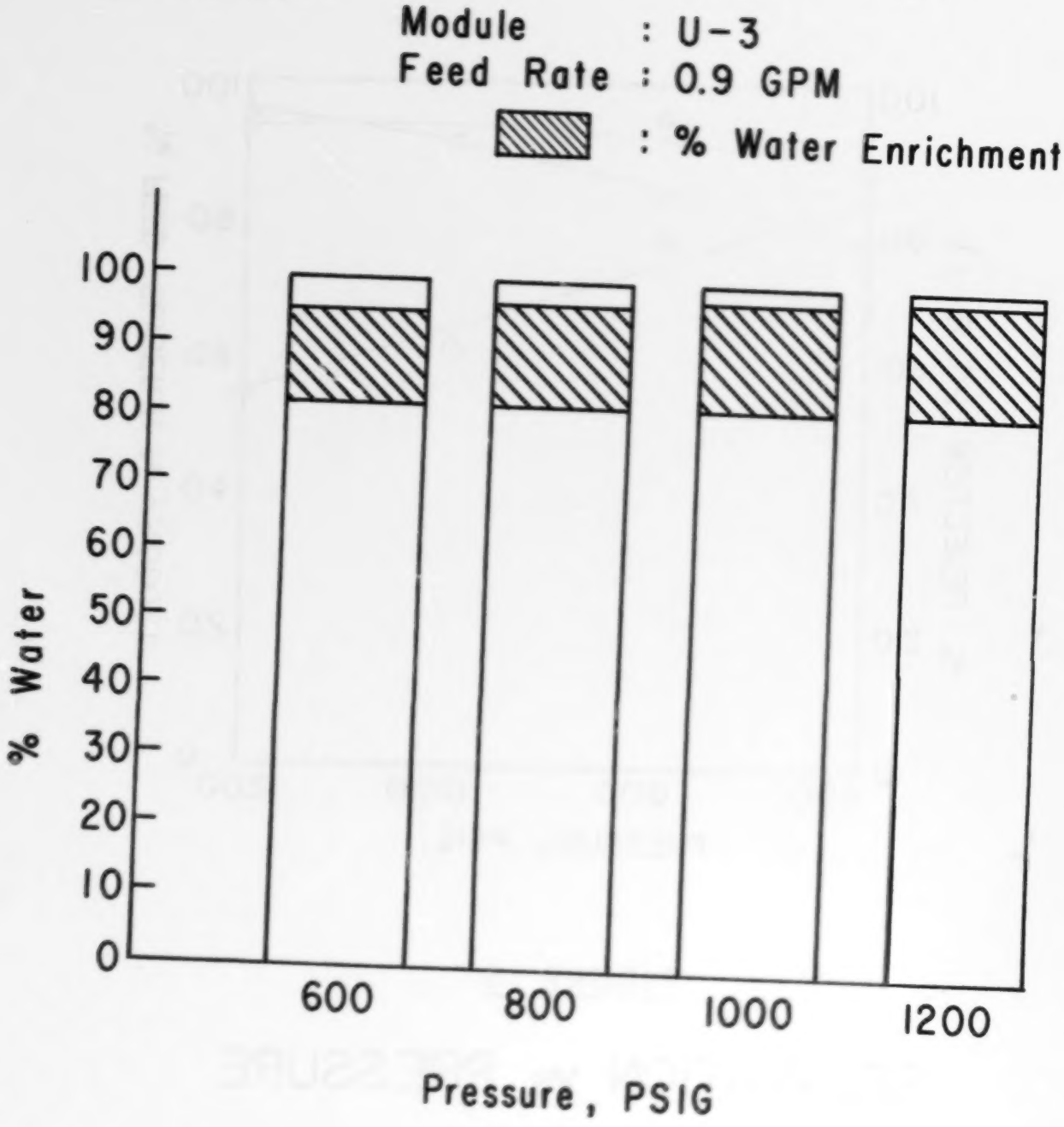
and an analogous one for inorganics:

$$S_i = (\%\ \text{Rejection of Inorganics} - \%\ \text{Rejection of Glycerin})$$

These parameters are indicative of the best separation of glycerin attainable. The separation factor does not, however, take into account productivity, so that this variable must be designated separately.

The data presented thus far on modules U-3 and AS-2 were also evaluated on the replacement module U-4. This unit exhibited a lower rejection for all of the solutes than U-3, but unfortunately did not compensate as well by increased flux. The effective osmotic pressure found by extrapolation of the J_w value to zero in Figure 6 is again found to be 160 psi. While these data would appear to be contradictory, i.e., lower flux and low rejection, they are in fact a consequence of the hydrodynamics of the process. Examination of the feed concentrations for the evaluation runs in Tables 6 and 8 reveals that the plant effluent under test differed in composition between the two trials. The U-4 module was in fact tested on a stream containing higher dissolved total solutes, vis. 23% compared to 18% for U-3. The determination that the same effective osmotic back pressure was operating with a much more concentrated feed stream indicates that the reflection coefficients must be lower for U-4 than for U-3. That this increased permeability does not result in increased flux will be shown to be the result of a marked increase in viscosity of the feed stream.

FIGURE - 5



WATER ENRICHMENT

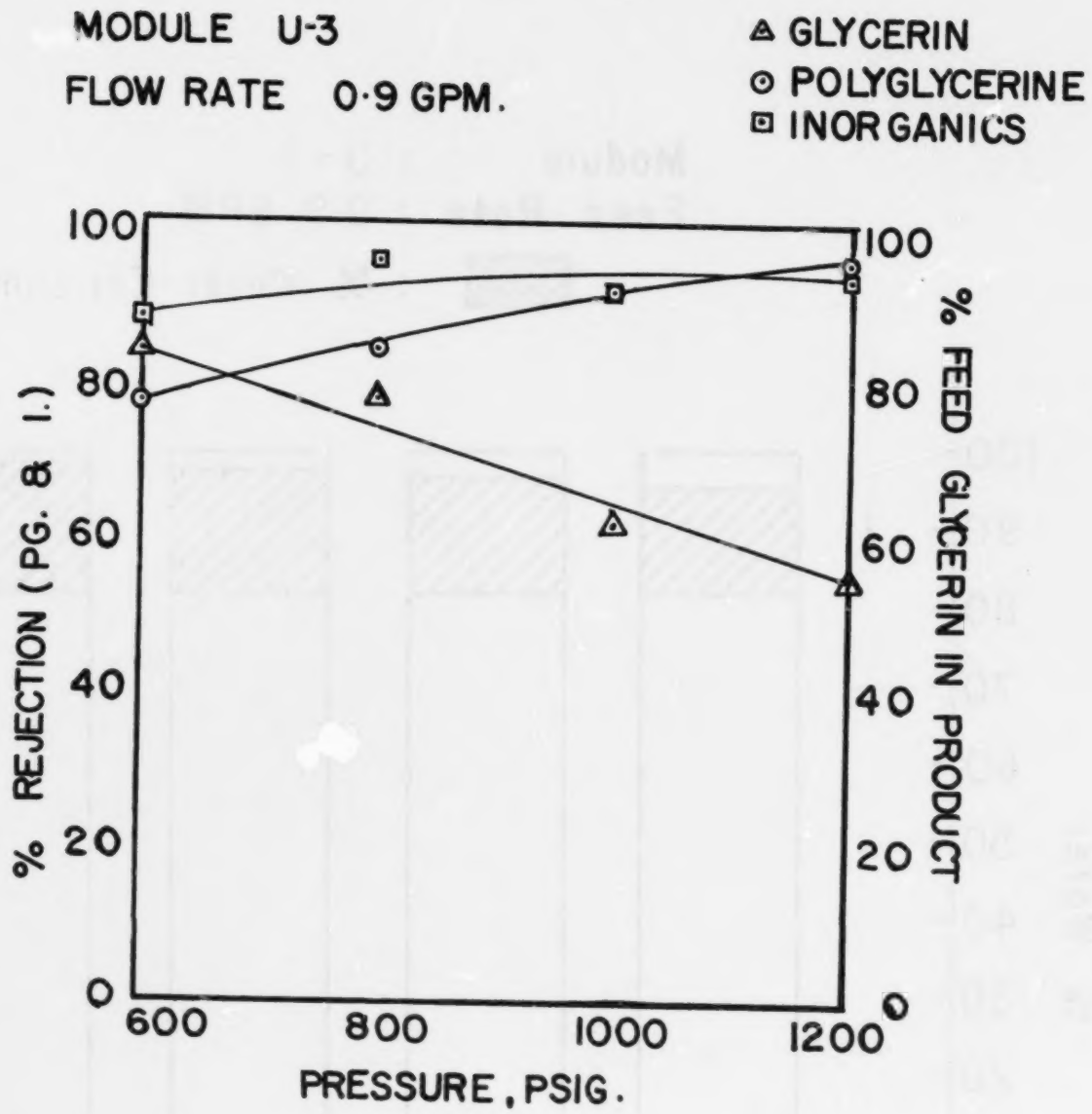


FIGURE - 6

SEPARATION vs PRESSURE

The significant factor found with U-4 was that a very concentrated multicomponent stream could indeed be separated by this technique, and with quite good efficiency. Using the index developed earlier, (S_o and S_i), the comparison of modules U-3, AS-2 and U-4 are shown in Table 11. It is apparent that the U-4 module is as effective in achieving separations as the original U-3, and that the loss of flux is related more to the hydrodynamics than to the membrane properties, per se.

TABLE - 11

SELECTIVITY INDICES FOR THE TUBULAR MODULES

Module No.	Pressure psig	Flux gfd	Selectivity S_o	S_i
U-3	800	5.20	62.1	73.0
AS-2	1000	2.47	30.2	26.1
U-4	700	1.98	61.4	66.6

A review of the tables presented thus far also indicates that the most effective separations are carried out at the lower rather than the higher operating pressures. Consequently, further studies concentrated on the pressures of 600-800 psi.

In examining the flux values for the several modules it is quite apparent that there was a significant decrease in going from a single solute at 10,000 ppm in water to the plant effluent. Part of the decrease at any given pressure is attributable to the back osmotic pressure, which has already been identified as varying from 160 to 450 psi. However, even if the pressures are corrected to reflect the osmotic forces there is still a reduction in flux compared to the single solute tests. Two reasons for this flux decline have been identified, and the steps necessary to combat the phenomenon can be outlined.

The crude plant stream was used without any filtration for the majority of the data reported. On microscopical examination during the program it was found that particulate matter was present in the stream, and can form a surface layer which can affect the flux rejection performance of the system. Some of this foreign material may arise from precipitation during the neutralization of the feed stream. The result of such fouling is that the effective area available for separation is reduced, and a parallel layer of a dynamically formed membrane is created. Prefiltration of the process stream through a 25 micron mesh filter was found to reduce this contamination significantly, but the fouling of the membrane had already been accomplished.

A second cause of flux reduction results from the increased viscosity of the feed stream due to the high solute concentrations. The

increase in viscosity reduced the turbulence and mixing at the solution-membrane interface. As the solvent permeates the membrane it leaves behind a layer of concentrated solution. If the turbulent mixing is inadequate to reduce the concentration in this layer to that of the bulk solution, the flux declines because the concentration gradient determining the osmotic back pressure (eqn 2) is that gradient which exists at each membrane interface. If the gradient increases, the osmotic back pressure increases, and the membrane "sees" a lower applied pressure. This phenomenon is termed concentration polarization, and is one of the most significant causes of flux decline in poorly designed systems. From the description given above it is evident that the magnitude of the concentration polarization is giverned by the geometry of flow, the velocity of flow, and by the membrane transport characteristics.

Effect of Feed Dilution on the Membrane Performance:

The concentration polarization described above can be reduced either by an increase in feed flow velocity, or by reduction of the feed stream viscosity. The temperature limitations for the membrane impose an upper limit to the lowering of solution viscosity which could be achieved through higher temperature operation, but dilution of the feed stream can effect significant lowering of the feed viscosity, and this avenue was explored in this project. The effect of diluting the effluent stream is exemplified by the data gathered with the U-4 module, and tabulated in Tables 12 through 18. The data are summarized in terms of the effect of dilution on the flux and on the selectivity index (S_o and S_i) in Table 19.

Another way of increasing mixing was by the incorporation of turbulence promoters into the tubes themselves. The AS-2 unit contained 7/16" diameter balls in the 1/2" inside diameter tubes. Localized velocities are increased significantly in this manner. A possible drawback to the use of such turbulence promoters is the potential that they may impact on the membrane surface and cause permanent damage. Additionally, the increased flow resistance creates a pressure drop down the length of the tube so that power is dissipated, with its attendant cost. The alternative - increased flow velocity through increased pump capacity - can be evaluated for each geometry under consideration. The mass transfer through the membrane and in the bulk solution is also effected by viscosity. It is not possible to separate the boundary layer problem from this phenomenon. The results indicate major improvements can be achieved by dilution.

The quantitative idea of the flux increase with dilution for the Module U-4 may be obtained from Table 18 and Figure 7, and it serves as an index for the measure of increase in flux. It is observed from Table 18 that a flux increase of more than four-fold is obtained with a 50% dilution. Appreciable flux increase (almost three-fold) was observed also at lower levels of dilution (30%). Lower viscosity and lower osmotic effect as a result of the dilution appear mainly responsible for the increased flux.

TABLE - 12

FLUX-PRESSURE-REJECTION (16% DILUTION) CHARACTERISTICS - 1

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

FEED : STREAM NO. 8

FLOW RATE : 1.0 gpm

No.	Pressure psig	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	400	1.71	Glycerin	2.19	2.10	4.1
			Polyglycerines	13.15	5.10	61.2
			Inorganics	2.26	0.67	60.4
			Water	82.40	92.13	-
2	600	2.84	Glycerin	2.07	1.91	7.7
			Polyglycerines	13.50	3.58	73.5
			Inorganics	2.35	0.41	82.6
			Water	82.08	94.10	-
3	700	3.34	Glycerin	2.14	1.80	15.9
			Polyglycerines	13.77	2.39	82.7
			Inorganics	2.40	0.28	88.3
			Water	81.69	95.53	-
~ 4	800	4.22	Glycerin	2.21	1.75	20.8
			Polyglycerines	15.58	3.99	74.4
			Inorganics	2.63	0.32	87.8
			Water	79.60	94.44	-

TABLE - 13

FLUX-PRESSURE-REJECTION (25% DILUTION) CHARACTERISTICS - 2

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

FEED : STREAM NO. 8

FLOW RATE : 1.0 gpm

No.	Pressure psig	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	500	3.56	Glycerin	1.63	1.46	10.4
			Polyglycerines	13.56	4.04	70.2
			Inorganics	2.17	0.40	81.6
			Water	82.70	94.10	-
~ 2	600	4.25	Glycerin	1.87	1.48	20.9
			Polyglycerines	13.00	2.93	77.5
			Inorganics	2.26	0.49	78.3
			Water	82.88	95.10	-
3	700	5.57	Glycerin	1.80	1.35	25.0
			Polyglycerines	12.99	2.31	82.2
			Inorganics	2.33	0.43	81.5
			Water	82.88	95.10	-
4	800	6.22	Glycerin	1.80	1.26	30.0
			Polyglycerines	13.24	2.06	84.4
			Inorganics	2.35	0.37	84.3
			Water	82.61	96.31	-

TABLE - 14

FLUX-PRESSURE-REJECTION (30% DILUTION) CHARACTERISTICS - 3

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

FEED : STREAM NO. 8

FLOW RATE : 1.0 gpm

No.	Pressure psig	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	500	3.86	Glycerin	1.65	1.39	15.8
			Polyglycerines	10.53	2.71	74.3
			Inorganics	2.01	0.46	77.1
			Water	85.81	95.44	-
2	600	5.02	Glycerin	1.61	1.34	16.8
			Polyglycerines	10.89	2.11	80.6
			Inorganics	2.03	0.30	85.2
			Water	85.47	96.25	-
3	700	6.39	Glycerin	1.64	1.28	22
			Polyglycerines	13.54	3.21	76.3
			Inorganics	2.11	0.27	87.2
			Water	82.71	95.24	-
4	800	6.65	Glycerin	1.57	1.18	24.8
			Polyglycerines	13.94	2.66	80.9
			Inorganics	2.15	0.22	89.8
			Water	82.34	95.94	-

TABLE - 15

FLUX-PRESSURE-REJECTION (40% DILUTION) CHARACTERISTICS - 4

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

FEED : STREAM NO. 8

FLOW RATE : 1.0 gpm

No.	Pressure psig	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	500	4.67	Glycerin	1.50	1.24	17.3
			Polyglycerines	9.96	2.02	79.7
			Inorganics	1.79	0.33	81.6
			Water	86.75	96.41	-
2	600	6.05	Glycerin	1.52	1.17	23
			Polyglycerines	10.07	1.63	83.8
			Inorganics	1.93	0.27	86.0
			Water	86.48	96.93	-
3	700	6.99	Glycerin	1.44	1.12	22.5
			Polyglycerines	10.30	1.38	86.6
			Inorganics	1.96	0.22	88.8
			Water	86.30	97.28	-
4	800	8.4	Glycerin	1.49	0.96	35.6
			Polyglycerines	11.24	1.33	88.2
			Inorganics	1.98	0.15	92.4
			Water	86.29	97.56	-

TABLE - 16

FLUX-PRESSURE-REJECTION (45% DILUTION) CHARACTERISTICS - 5

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

FEED : STREAM NO. 8

FLOW RATE : 1.0 gpm

No.	Pressure psig	Flux		Feed Composition % w	Product Composition % w	Rejection %
1	500	5.75	Glycerin	1.27	1.01	20.5
			Polyglycerines	9.77	2.35	75.9
			Inorganics	1.72	0.28	83.7
			Water	87.24	96.36	-
2	600	6.52	Glycerin	1.09	0.94	13.9
			Polyglycerines	10.38	1.68	83.8
			Inorganics	1.92	0.32	83.3
			Water	86.61	97.06	-
3	700	8.1	Glycerin	1.29	0.83	35.7
			Polyglycerines	10.05	1.11	89.0
			Inorganics	1.74	0.13	92.5
			Water	86.92	97.93	-
4	800	9.09	Glycerin	1.43	0.69	51.7
			Polyglycerines	9.96	1.01	89.9
			Inorganics	1.78	0.10	94.4
			Water	86.83	98.2	-

TABLE - 17

FLUX-PRESSURE-REJECTION (50% DILUTION) CHARACTERISTICS - 6

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

FEED : STREAM NO. 8

FLOW RATE : 1.0 gpm

No.	Pressure psig	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	500	5.55	Glycerin	1.13	0.82	27.4
			Polyglycerines	8.84	1.66	81.2
			Inorganics	1.58	0.19	88.0
			Water	88.35	97.33	-
2	600	6.72	Glycerin	1.08	0.83	23.1
			Polyglycerines	9.21	1.17	87.3
			Inorganics	1.56	0.11	92.9
			Water	88.15	97.89	-
3	700	8.7	Glycerin	0.92	0.70	23.9
			Polyglycerines	9.15	0.98	89.3
			Inorganics	1.57	0.07	95.5
			Water	88.36	98.25	-

TABLE - 18

FLUX INCREASE WITH DILUTION

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

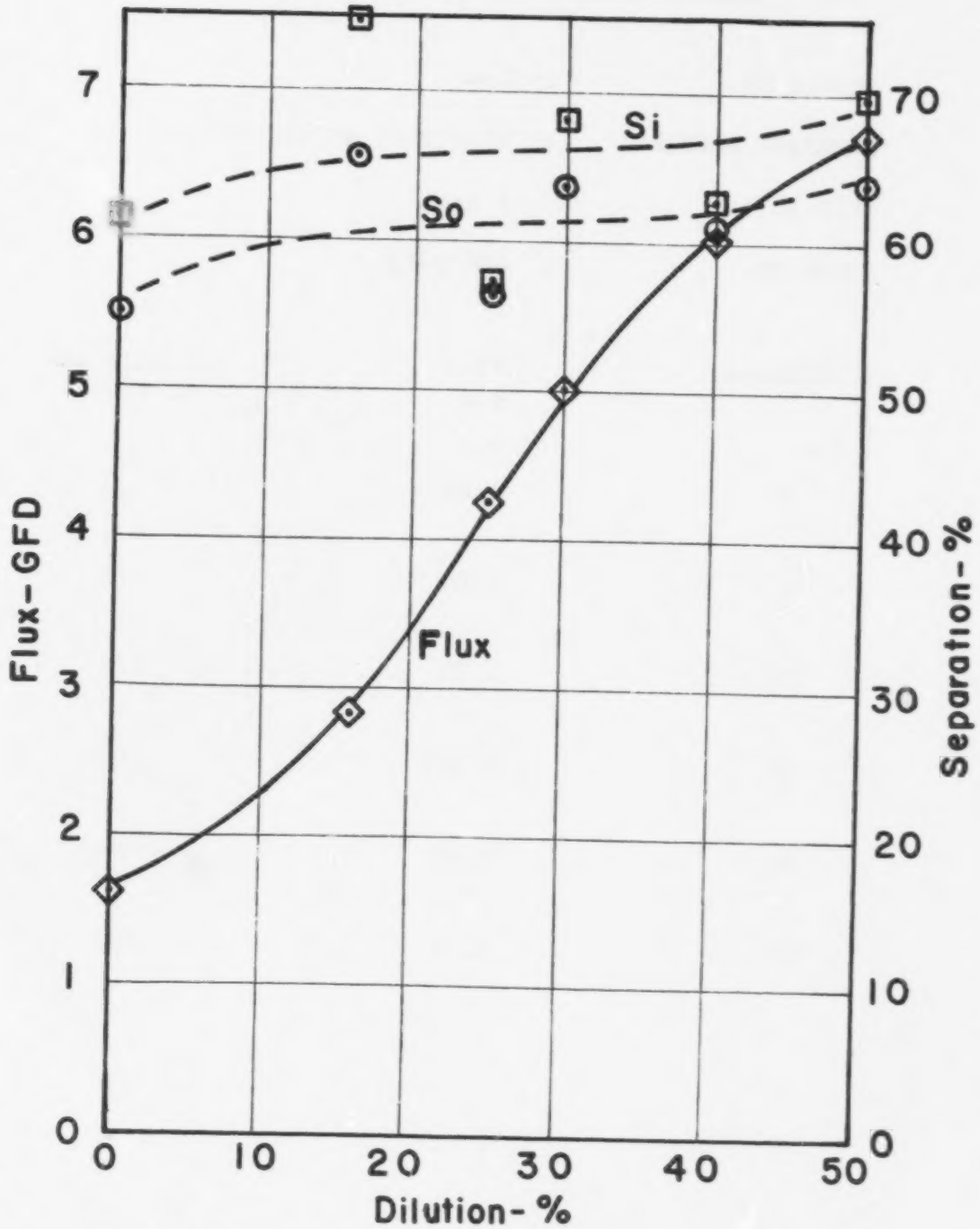
FEED RATE : 1 gpm

PRESSURE : 600 psig

No.	% Dilution	Flux gfd	% Increase in flux
1	0	1.66	0
2	16	2.84	71
3	25	4.25	156
4	30	5.02	202
5	40	6.05	264
6	50	6.72	305

Module - U4

Flow Rate - 1 gpm



Dilution versus Performance

FIGURE - 7

TABLE - 19

EFFECT OF DILUTION ON FLUX-PRESSURE-REJECTION RELATIONSHIPS

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

FEED RATE : 1 gpm

Pressure	16% Dilution			25% Dilution			30% Dilution			40% Dilution			45% Dilution			50% Dilution		
	Flux	S_o	S_i	Flux	S_o	S_i	Flux	S_o	S_i	Flux	S_o	S_i	Flux	S_o	S_i	Flux	S_o	S_i
400	1.7	56	57	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
500	-	-	-	3.6	71	60	3.9	61	58	4.7	65	63	5.8	64	56	5.6	61	54
600	2.8	75	66	4.3	57	56	5.0	68	64	6.1	64	61	6.5	70	70	6.7	71	65
700	3.3	74	74	5.6	57	57	6.4	65	54	7.0	66	64	8.1	58	53	8.7	70	65
800	4.2	68	57	6.2	54	54	6.7	65	57	8.4	57	53	9.1	42	38	9.9	-	-

The Effect of Feed Flow Rate on Membrane Performance:

The effect of feed flow rate on the performance of module U-4 was studied. The range of variation of the feed flow rate was 0.5 to 1.0 gpm at 600 psig. The results are plotted in Figure 8 as flux; S_o, and S_i (defined earlier) vs. feed flow rate.

The flux increased from 4.8 gfd at 0.5 gpm to 7.0 gfd at 0.95 gpm exponentially. No definite trend was, however, noticed with respect to rejections and, therefore, S_o and S_i.

The flux increase could be explained on the basis of concentration polarization effect studied extensively by several writers (8, 9, 10). The concentration polarization (which is a strong function of feed concentration and feed viscosity) decreases with higher feed rates due to better mixing conditions at the membrane-feed solution interface. This consequently improves the effective driving pressure for the system and hence the increase in flux. The lack of any such trend with rejections is hard to explain with the limited data at hand, especially within the very narrow range of change of feed flow rate studied here.

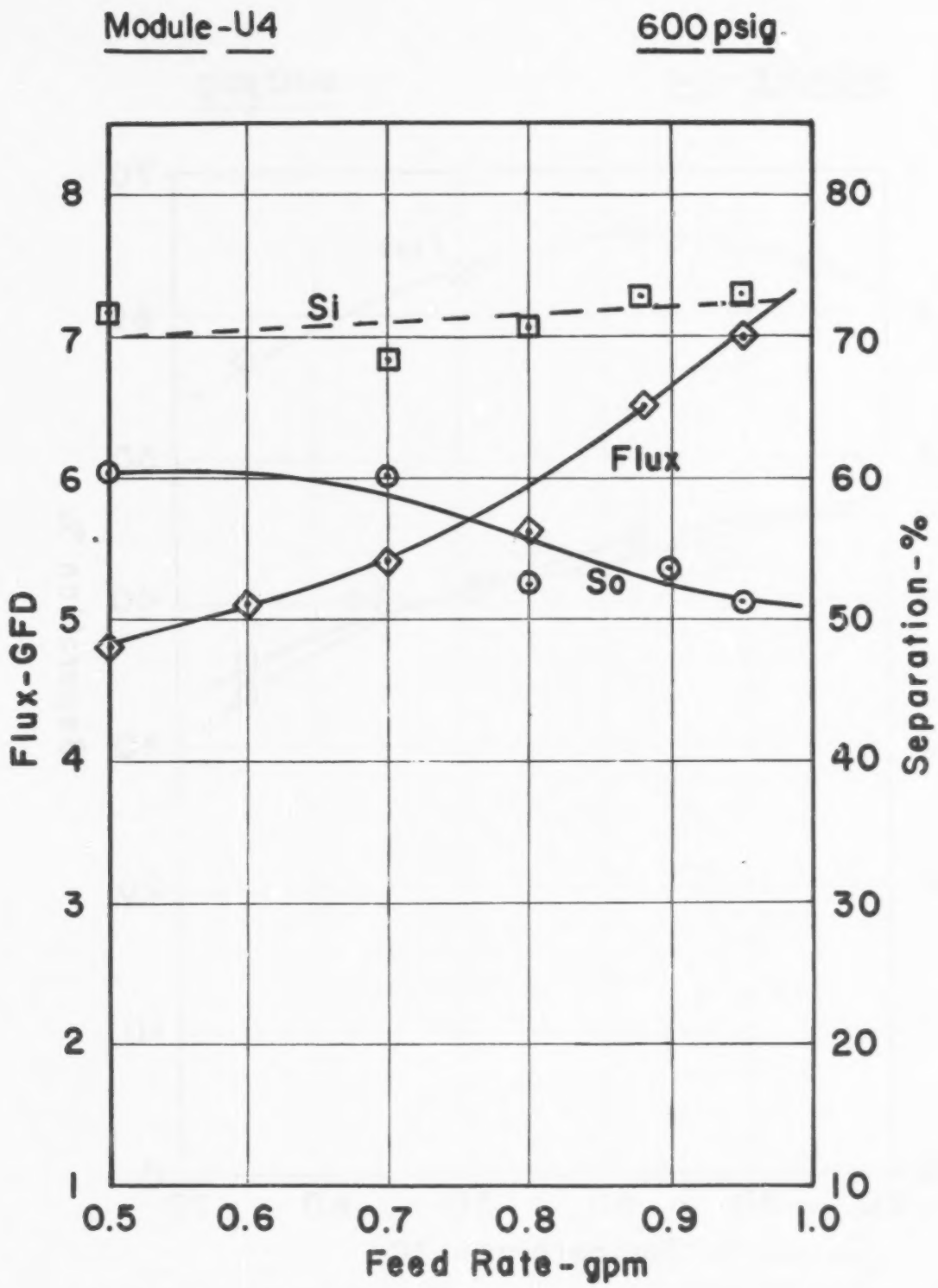
The feed flow rate was limited to one gallon per minute for the present experiments due to the limitation of the pilot unit. Parts to modify the unit, in order to obtain higher feed flows, were ordered during the grant period. However, these parts were not received in time to make the necessary modifications and to include higher feed rates as a part of this study. The data does, however, indicate that additional increases in flux might be achieved at flow rates exceeding one gallon per minute.

The Effect of Temperature on Membrane Performance:

The effect of feed temperature on the performance of module U-4 was studied at a constant feed rate of 0.9 gpm and a pressure of 600 psi. The feed solution was subjected to temperature increase from 20°C to 70°C. The results are plotted in Figure 9 as Flux, S_o and S_i versus the feed temperature.

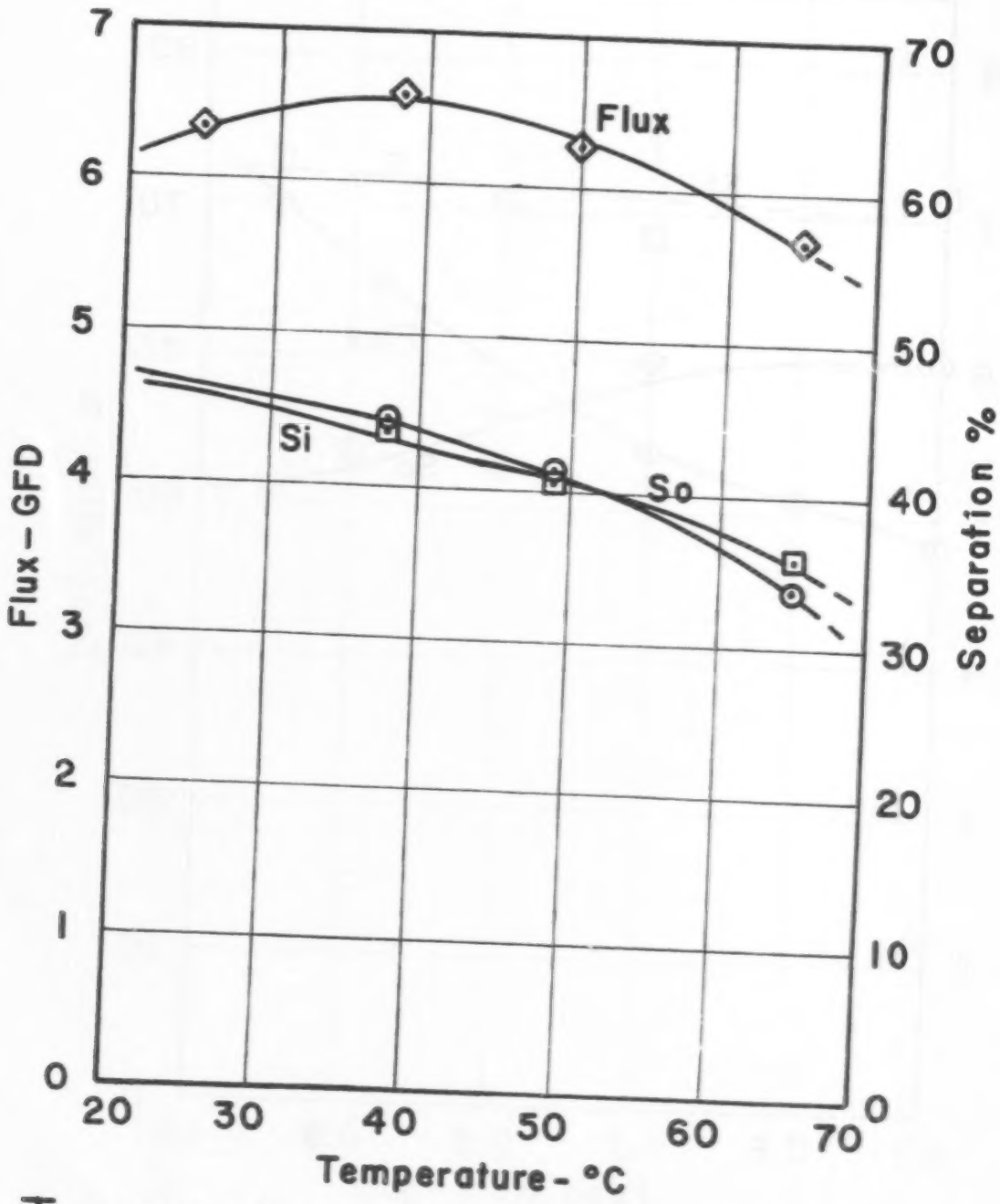
The flux increased initially with temperature reaching a maximum of 6.6 gfd at about 38°C and then decreased gradually to 5.7 gfd at 65°C. The selectivity indices S_o and S_i decreased steadily with an increase in temperature. The changes in these membrane properties were found irreversible with temperature.

This response is not surprising considering the level of solutes present in the feed solution. It has been well established that in pure water, cellulose acetate membranes undergo a glass transition around 75°C. This is a lowering of the same transition that occurs in the dry membrane by approximately 100°C. The lowering in the transition tempera-



Feed Flow versus Performance

FIGURE - 8



Temperature versus Performance

FIGURE - 9

ture is attributed to the plasticization that occurs in the presence of water. Glycerin is a better plasticizer than water and, therefore, the glass transition in the system under study should occur at a temperature even lower than that with water. The data shows the glass transition temperature in the present case to be close to 38°C. The drop in the flux and selectivities S_o and S_i is due to the change in the membrane morphology (reduction in the porosity) above the glass transition temperature. The initial increase in the flux is believed to be related to the lowered viscosity of the feed with increased temperature.

Multistage Treatment:

The product from a single stage treatment still contains significant amounts of organic and inorganic constituents to be returned to the process unit. A multistage treatment was considered to overcome this problem and, therefore, several two-stage treatment studies were made. The same membrane module was used in the first and the second stage. The membranes were selected on the basis of maximum separation for a one pass system and, therefore, may not be the best choice for the second and subsequent stages. The efficiency of the system, however, should be adequate to demonstrate the advantages of such a treatment.

Modules AS-2 and U-4 were subjected to two-stage runs at 1,000 and 600 psig respectively. The flow scheme for these runs involved stepwise concentration of the diluted feed (Tables 20 and 22) by raffinate recycle in the first stage, followed by another stepwise concentration of the combined first stage product to obtain the final product (Tables 21 and 23) in the second stage. Samples were drawn approximately every three hours in the first stage and approximately one and one-half hours in the second stage. The run duration was, thus, about twelve hours for the first stage and about six hours for the second stage.

The Module U-4 exhibited better selectivity over Module AS-2. The selectivity is mainly dependent on the membrane structures, however, to an extent, this was also due to the differences in the feed compositions. The feed to U-4 was lower in total solute concentration. The turbulence promoter containing Module AS-2, however, offered a higher flux, notwithstanding the higher rejection characteristics, when compared with Module U-4. The lower viscosity (resulting mainly from the lower total solute concentration in the feed) and a higher level of turbulence (brought about by the turbulence promoters) are believed to be responsible for this performance.

TABLE - 20

FIRST STAGE RUN

MODULE NO. : AS-2

MEMBRANE SOURCE : AMERICAN STANDARD

FEED : STREAM NO. 8 (INITIAL DILUTION 60%)

FLOW RATE : 0.9 gpm

PRESSURE : 1000 psig

No.	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	22.2	Glycerin	0.56	0.18	67.9
		Polyglycerines	5.43	0.16	97.1
		Inorganics	1.14	0.04	96.5
		Water	92.87	99.62	-
2	19.7	Glycerin	0.73	0.25	65.8
		Polyglycerines	6.72	0.16	97.6
		Inorganics	1.45	0.06	95.9
		Water	91.10	94.53	-
3	16.8	Glycerin	0.92	0.23	75.0
		Polyglycerines	8.54	0.32	96.3
		Inorganics	1.80	0.08	95.6
		Water	88.74	99.37	-
4	13.25	Glycerin	1.04	0.30	71.2
		Polyglycerines	7.63	0.51	93.3
		Inorganics	2.24	0.13	94.2
		Water	86.09	99.06	-

TABLE-21

SECOND STAGE RUN

MODULE NO. : AS-2

MEMBRANE SOURCE : AMERICAN STANDARD

FEED : STREAM NO. 8 (COMBINED FIRST STAGE PRODUCT)

FLOW RATE : 0.9 gpm

PRESSURE : 1000 psig

No.	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	34.7	Glycerin	0.20	0.07	65.0
		Polyglycerines	0.30	0.02	93.3
		Inorganics	0.08	0.01	87.5
		Water	99.42	97.90	-
2	34.1	Glycerin	0.22	0.09	59.1
		Polyglycerines	0.40	0.02	95.1
		Inorganics	0.09	0.01	88.9
		Water	99.29	99.89	-
3	28.4	Glycerin	0.23	0.09	60.9
		Polyglycerines	0.57	0.02	96.5
		Inorganics	0.10	0.01	90.0
		Water	99.20	99.87	-
4	17.3	Glycerin	0.28	0.09	67.9
		Polyglycerines	0.73	0.10	86.3
		Inorganics	0.15	0.01	93.3
		Water	99.89	99.89	-

TABLE - 22

FIRST STAGE RUN

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

FEED : STREAM NO. 8 (INITIAL DILUTION 50%)

FLOW RATE : 1.0 gpm

PRESSURE : 600 psig

No.	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	8.25	Glycerin	1.02	0.73	28.4
		Polyglycerines	8.30	1.31	84.2
		Inorganics	1.48	0.19	87.2
		Water	89.20	97.77	-
2	5.91	Glycerin	1.13	0.87	23.0
		Polyglycerines	10.75	1.67	84.5
		Inorganics	2.04	0.19	90.7
		Water	86.08	97.27	-
3	3.42	Glycerin	1.19	0.98	17.7
		Polyglycerines	11.77	2.22	81.1
		Inorganics	2.37	0.31	86.9
		Water	83.65	96.49	-
4	1.59	Glycerin	1.25	1.13	9.6
		Polyglycerines	16.29	4.09	74.9
		Inorganics	3.20	0.51	84.1
		Water	79.26	94.27	-

TABLE - 23

SECOND STAGE RUN

MODULE NO. : U-4

MEMBRANE SOURCE : UNIVERSAL WATER CORP.

FEED : STREAM NO. 8 (COMBINED FIRST STAGE PRODUCT)

FLOW RATE : 1.0 gpm

PRESSURE : 600 psig

No.	Flux gfd		Feed Composition % w	Product Composition % w	Rejection %
1	19.0	Glycerin	0.82	0.55	32.9
		Polyglycerines	2.27	0.65	71.4
		Inorganics	0.16	0	100.0
		Water	96.75	98.8	-
2	16.6	Glycerin	0.91	0.57	37.4
		Polyglycerines	2.81	0.83	70.5
		Inorganics	0.23	0	100.0
		Water			
3	16.6	Glycerin	0.97	0.70	27.8
		Polyglycerines	3.33	1.14	65.8
		Inorganics	0.31	0.04	87.1
		Water	95.39	98.12	-
4	15.5	Glycerin	0.97	0.70	27.9
		Polyglycerines	3.33	1.14	65.8
		Inorganics	0.31	0.04	87.1
		Water	95.39	98.12	-

Projection to Plant Scale Operation:

A projected plant-scale operation can be assembled from the laboratory experimental results, using the data from the U-4 module, operated at 600 psig with a feed diluted 40% with water as a base point. The dilution of the feed, as mentioned in the preceding section, improves the flux through the membrane but at a cost of glycerin concentration in the membrane-permeated product (this may lead to an increased distillation cost in some systems).

Three different models are depicted to illustrate the recovery of glycerin from the waste stream using both single stage and multi-stage operation. Various other alternatives are possible depending on the specification of the final extract composition and characteristics of the membranes employed, however these three will demonstrate the applicability of the technique of Reverse Osmosis to the treatment of glycerin waste streams. The three models are:

i) Single stage operation;

ii) Multistage operation with forward feed;

iii) Multistage countercurrent operation.

The basis of calculations for all three models is based on the data shown in Tables 20 through 23,and an undiluted feed rate of 10 gallons per minute. The feed composition (percent by weight) of this undiluted waste stream is shown below:

Water	76%
Polyglycerine	18%
Glycerin	3%
Inorganics	3%

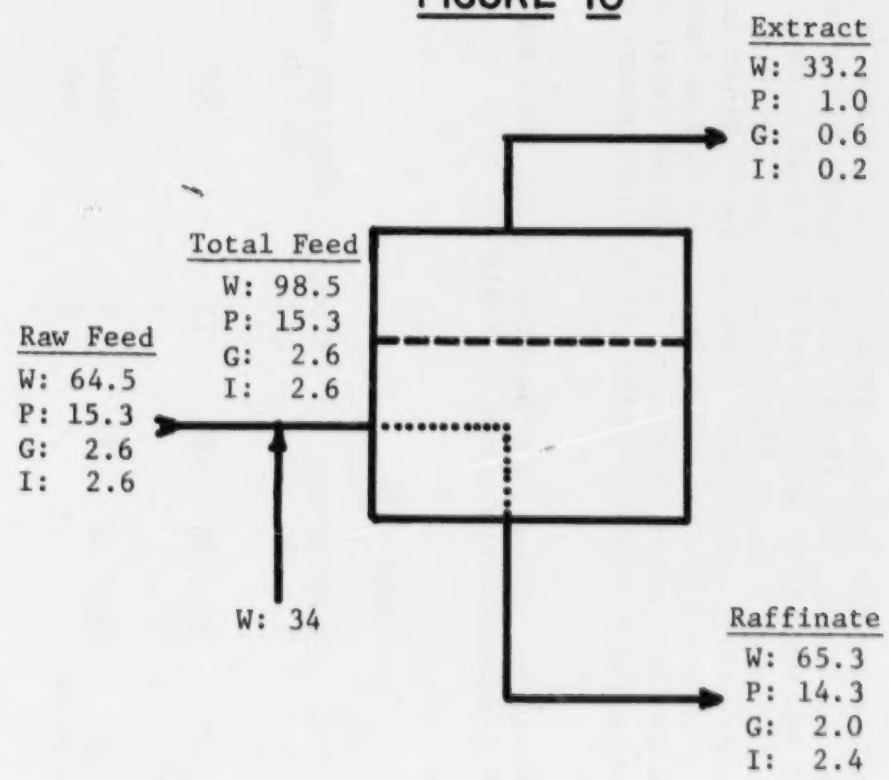
The average values of membrane flux and rejection were estimated from experimental data using a linear intergration of these parameters as a function of viscosity and membrane area. Figure 7. illustrates that such an estimate should yield a conservative value for flux. The membrane area was selected based on a design philosophy to remove the water of dilution.

Single Stage Operation:

Figure 10 shows the single stage material balance for glycerin recovery operating at 600 psig and with a 10 gpm (approximately 85 lbs. per minute) raw feed rate and a 4 gpm (approximately 34 lbs. per minute) water added for the reduction of the feed stream viscosity.

W,P,G,I : lbs./min.

FIGURE-10



SINGLE STAGE OPERATION

Under these conditions the average flux through the membrane is estimated to be 5 gallons/ft^2/day. Employing 1200 square feet of membrane area and assuming the rejection ratios to be Glycerin 22%, Polyglycerin 78%, Inorganics 78%, as determined in the experimental test, the water of dilution can be recovered; in addition to 10% of the raw feed water. This recovered product contains 27% of the recoverable glycerin along with a small percentage of the original polyglycerin and inorganics. For some systems this product stream from a single stage separation may be adequate for recycle. However, in the particular system under study the deleterious effects of the inorganics in the glycerin distillation require their complete removal. This can be accomplished in a multistage operation.

Multistage Operation with Forward Feed:

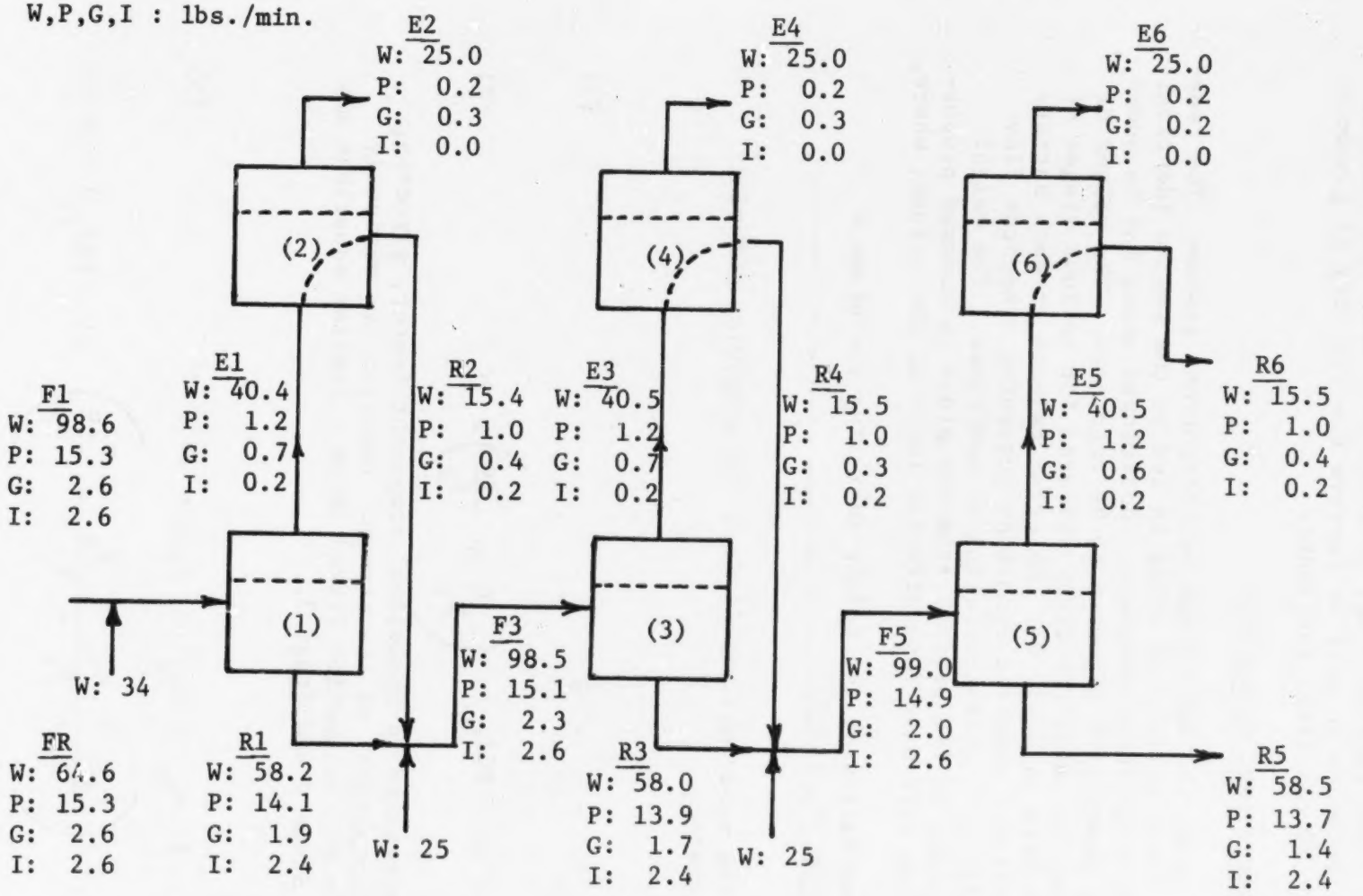
In a multistage operation the product from the first stage is processed through a second stage. The first stage product has a low total dissolved solids concentration and, therefore, the flux rate in the second stage is much higher than in the first stage. In this particular model the raffinates from stages 1 and 2 are combined and diluted with water to obtain a solution viscosity close to the feed to the first stage. This new stream, F_3 in Figure 11, is then treated in the same manner and the process repeated until the desired amount of glycerin is recovered.

The values of rejections, fluxes, and membrane areas that are used in the multistage treatments are shown in Table 24.

TABLE - 24

Multistage Model	Stage No.	% Rejection G	P	I	Flux, gfd	Membrane Area Sq. Ft.
Forward Feed Countercurrent	2, 4, 6 1A,1B	33	66	100	15	300
Forward Feed	1, 3, 5	22	78	78	5	1440
Countercurrent	2A,3A,2B,3B				4	1440

G, P, and I stand for glycerin, polyglycerine, and inorganics. The material balance shown in Figure 11 reflects the performance obtainable with this system. Addition of water between each stage is necessary to maintain favorable stream viscosity. However, the design of the recovery unit is based on reclaiming most of the added water along with the valuable constituent,glycerin. The three units shown indicate the decreasing trend in the recovery of glycerin with



MULTISTAGE FORWARD FEED OPERATION

FIGURE - II

the addition of more units. The schematic representing this model in Figure 11 is an open system to leave the choice of installing additional units open as per the dictation of process economics and pollution standards for an individual application. In an actual plant installation the final raffinate R_6, would be recycled. The raffinate R_5 could also be recycled in part to improve the recovery of glycerin and concentration of the final raffinate.

Multistage Countercurrent Operation:

Figure 12 shows the multistage countercurrent system. The reaffinate from the first battery of cells is fed to the second identical battery for further glycerin recovery. Additional units may be added depending on the amounts of glycerin to be recovered. The values of rejections, fluxes and membrane areas selected for various stages of this model are listed in Table 24. Material balance on each battery is obtained by solving algebric equations governing component flow rates and the rejection characteristics of membranes. The weight fraction of a solute in the product from any stage is assumed proportional to the mean raffinate concentration (mrc) of the solute, where,

$$\text{mrc} = \frac{\text{concentration of the solute (entering the stage + leaving the stage)}}{2}$$

The following equations result from the stagewise material balance of the system.

Stage - 1:

$$e_{2c} - e_{1c} - r_{1c} = 0 \tag{3}$$

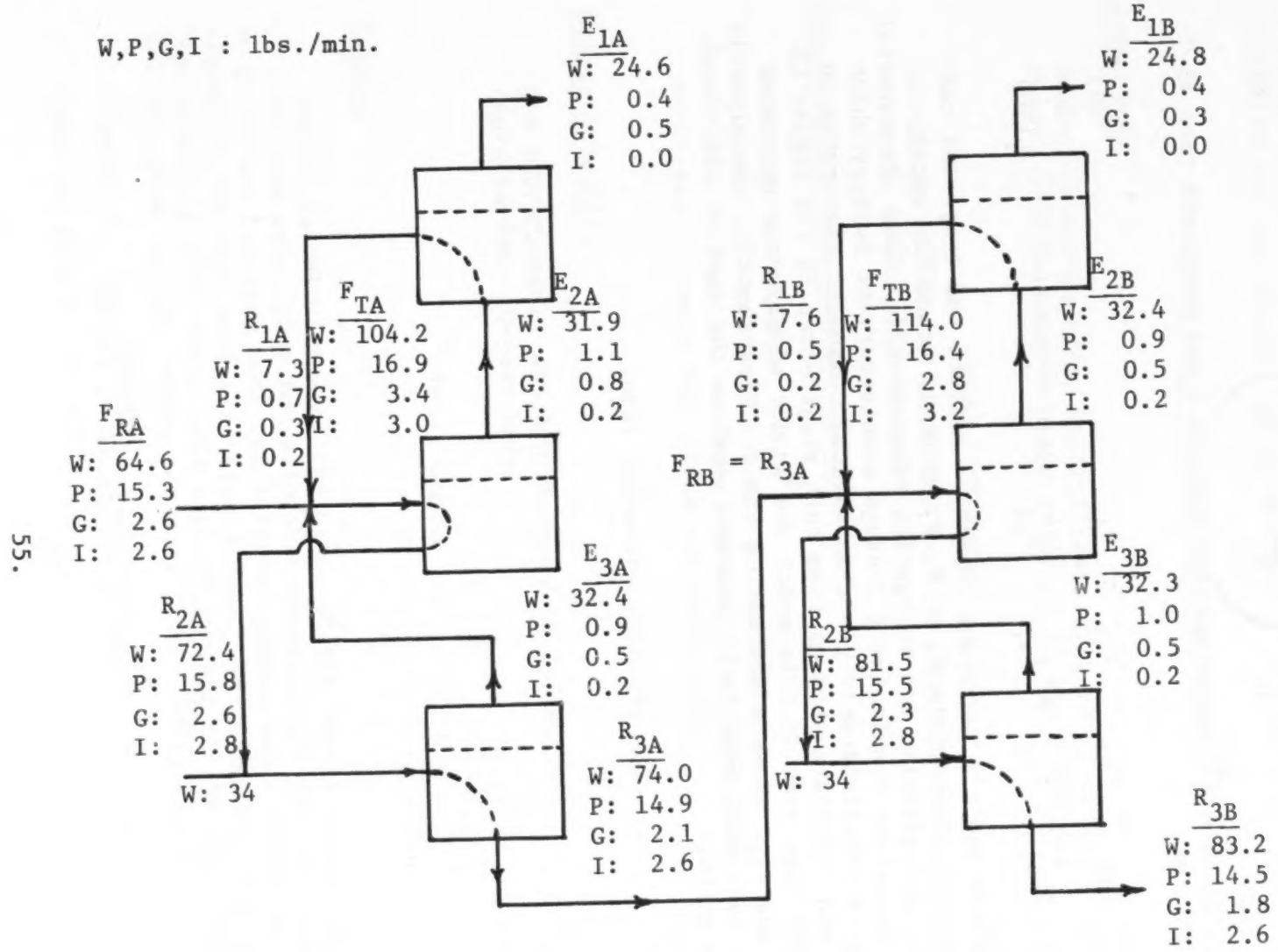
$$\frac{e_{1c}}{E_1} - 1/2\ (1 - REJ_{1c}) \left(\frac{r_{1c}}{R_1} + \frac{e_{2c}}{E_2}\right) = 0 \tag{4}$$

Where c represents an individual component (water, glycerin, polyglycerin, inorganics) of the stream. Equation (4) obviously results from the mrc assumption listed above. Similar equations may be written for Stage 2 and Stage 3.

Stage - 2:

$$f_c + r_{1c} + e_{3c} - r_{2c} - e_{2c} = 0 \tag{5}$$

$$\frac{e_{2c}}{E_2} - 1/2 \left(\frac{r_{1c} + e_{3c} + f_c}{R_1 + F_3 + F} + \frac{r_{2c}}{R_2}\right) (1 - REJ_{2c}) = 0 \tag{6}$$



MULTISTAGE COUNTERCURRENT OPERATION

FIGURE - 12

Stage - 3:

$$r_{2c} - e_{3c} - r_{3c} = 0 \qquad (7)$$

W is added to the right hand side of equation (7) when expressing water balance on Stage 3.

$$\frac{e_{3c}}{E_3} - 1/2 \quad (1 - REJ_{3c}) \left(\frac{r_{ec}}{R_3} + \frac{r_{2c}}{R_2+W} \right) = 0 \qquad (8)$$

Also, for the i^{th} stage extract rate (E_1) and raffinate rate (R_i) are defined as:

$$E_i = e_{iw} + e_{ia} + e_{ip} + e_{il} \qquad (9)$$

$$R_i = r_{iw} + r_{ig} + r_{ip} + r_{il} \qquad (10)$$

Where e's and r's represent component extract and component raffinate rates. Subscripts W, G, P, I, as usual stand for water, glycerin, polyglycerin and inorganics respectively. Thus 24 material balance equations result for a 3-stage countercurrent battery which when solved simultaneously yield individual component flow rates in extract and raffinate streams from each stage shown in the Figure 12. It is seen that even in this model the amount of glycerin recovered (in E_{1A} and E_{1B}) shows a decreasing trend. Consequently, the glycerin recovery cost will have to be balanced against the cost of additional membrane units.

Economic Analysis:

Each potential plant would require its own economic analysis. Preliminary economic estimations may, however, be made based on the mass balance, obtained for the three models discussed. The estimate is worked out in detail for the multistage forward feed model as an illustration. Results for the other two models, obtained identically, are listed in Table 25. Engineering economics texts (11, 12) are referred to for the estimation procedures.

Multistage Forward Feed Operation

Investment:

Membranes and modules, initial cost, 5200 ft^2 @ \$25/ft^2	\$130,000
Pumps, 3-10 horsepower pumps rated at 15 gpm @ 600 psi	3,600
Total Investment	\$133,600

(assume no additional distillation cost; piping ignored; controls included in above)

Operating Expenses (Annual basis):

Membrane Maintenance \$2/ft^2	10,400
Manpower 1/4 man @ \$8,500 for 4 shifts plus .8 shifts to cover vacation, holidays, etc.	10,200
Utilities Power \$70, Steam and Water free	100
Total Operating Expenses	\$20,700

Glycerin Credit:

0.8 lbs/minute or 415,000 lbs/year \$0.15/lb.	62,250
Depreciation 10-year base	13,360
Total Credit	\$75,610

Payout:

Payout is calculated on the basis of the annual return diminished by a 48% tax rate, plus the allowable depreciation (10 year basis). No provision has been made for interest costs, since these can be included in the risk analysis calculations. For examples, the capital requirement of \$133,600 is paid back by the sum of the depreciation \$, \$13,360 plus the net return per year (100 - 48%)(\$41,550), or

$$\text{Payout} = \frac{133{,}600}{(0.52) \times (41{,}550) + 13{,}360} = 3.8 \text{ years}$$

Rate of return = 26%

TABLE - 25

ECONOMIC ESTIMATION

	Single Stage	Multistage Forward Feed	Multistage Countercurrent
Total Investment	33,600	133,600	163,600
Total Operating Expenses	12,650	20,700	23,300
Glycerin Credit	46,650	62,250	62,250
Payout Time, Years, Months	1 Yr.,7 Mos.	3 Yrs.,9 Mos.	4 Yrs.,6 Mos.
% Rate of Return	62.5	26	22

It is observed from Table 25 that complete removal of inorganics raises the total investment appreciably and, therefore, results in a much lower rate of return. The economics is thus very sensitive to the level of removal of inorganics.

The cost of neutralization of the waste stream is not included in this estimation since many plants may have some dispensable neutralizing streams. For the particular stream studied in this report the pH of the feed stream varied between 8 and 9. Based on pH 9 of the waste stream, the cost of neutralization with phosphoric acid is estimated to be less than $2,000/year.

The predominant item in this analysis is the membrane investment and the maintenance cost. We have deli erately chosen costs for these parameters higher than the normally reported valued in the literature. To cite an example, most analyses report a membrane maintenance cost of $0.60 to $1.00 per square foot per year as against the $2.00 per square foot per year assumed here. The life expectancy of membranes in the glycerol system remains to be established, therefore, a conservative figure was used in this cost summary. Similarly, the initial investment cost was based on a small pilot unit, and should be less for larger installations.

Major savings can be achieved in the process if the total membrane area can be reduced. This study indicates that flux through the membrane can be increased by increased turbulence, reduced viscosities, and prefiltration to remove suspended matter and/or high molecular weight species. Since the required membrane area is inversely proportional to the flux, a 25% increase in flux would result in a similar reduction in the required membrane area. The payout in years would correspondingly be reduced to about 2.9 years with a 34% for forward feed operation and 3.4 years with a return of 29% for the countercurrent operation. The data in this study indicate an improvement of this magnitude or greater, and should be attainable with an additional investigation.

Section VI

PROPYLENE GLYCOL WASTE STREAM (Dow Chemical Company)

During the period of the present grant, The Dow Chemical Company, Freeport, Texas, also had an R&D grant from FWQA for the investigation of various methods for disposal of a waste stream from their propylene glycol production plant (Project No. 12020 EEQ). In establishing the best disposal system for this stream, Dow and FWQA requested Gulf South Research Institute to study reverse osmosis as one of the methods having potential to aid in the solution of this problem. The waste stream had the following composition:

NaCl %	9.3 - 10.4
Propylene Glycol ppm	500 - 2000
Propylene Chlorohydrin ppm	20 - 70
Propylene Oxide ppm	100 - 500

It was indicated that it would be desirable to reduce the NaCl concentration to less than 1% (in the product) while increasing the propylene glycol concentration to greater than 1%.

Several problems were apparent for the application of reverse osmosis technique to this stream. First, the propylene glycol and NaCl molecules do not differ appreciably in size. In those systems where there is a large difference in the average diameter of the solutes, the separation by reverse osmosis is relatively simple. However, as the solutes approach the same size, the task becomes more formidable. Second, the high salt content of this stream further complicates the problem due to a very high osmotic pressure in a system with semipermeable membranes. Separation under these conditions can occur only if preferential interaction of solutes in the system occurs within the membrane phase. Based on this hypothesis,several membranes were examined for their ability to effect separations.

Both flat plate cells, where a number of candidate membranes could be screened, and the tubular module described in the preceding sections were used for evaluation. The data are presented in Tables 26 and 27. The results show that among these membranes the maximum selectivity was offered by the membrane G-23; however, even this was far from adequate. This may be due to the fact that when a membrane is selected with low enough NaCl rejection to reduce the osmotic effect to an acceptable level, pore flow becomes a dominant mode of transfer and, therefore, very little separation of solutes is observed.

The preliminary tests thus showed that reverse osmosis did not appear to be a very promising technique for the treatment of this stream. Further investigation was, therefore, discontinued.

TABLE - 26

DOW WASTE STREAM - I

MEMBRANE : CELLULOSE ACETATE (EASTMAN)

MEMBRANE GEOMETRY : FLAT SHEET

PRESSURE : 800 psi

ANALYSIS : DOW CHEMICAL COMPANY, FREEPORT, TEXAS

Membrane	INORGANIC Flux gfd	Feed Weight %	Prod. Weight %	Rej. %	ORGANIC Flux gfd	Feed ppm	Prod. ppm	Rej. %
G-16	54.5	9.1	8.6	5.5	54.5	1600	1600	0
G-17	35.1	9.1	7.7	15.4	35.1	1600	1610	0
G-19	29.5	9.2	7.3	20.7	29.5	1800	1440	20
G-20	41.1	9.2	8.0	13.0	41.1	1800	1680	6.7
G-21	21.1	10.0	7.9	21.0	21.1	1610	1650	0
G-22	23.5	10.0	8.0	20.0	23.5	1610	1560	3.1
G-23	10.5	10.1	6.5	35.6	10.5	1890	1640	13.2
G-24	35	10.1	8.3	17.8	35	1890	1680	12.5
G-25	12.4	9.4	5.1	55.7	12.4	2040	1202	41

TABLE - 27

DOW WASTE STREAM - II

MEMBRANE	:	CELLULOSE, GSRI, B-112
MEMBRANE GEOMETRY	:	TUBULAR
PRESSURE	:	600 psi
FLOW RATE	:	0.85 gpm

Test	Feed Composition(1)	Hours of Operation	Flux gfd	Rejection %
1	10.2% Sodium Chloride			9.5
	876 ppm Propylene Glycol	1	7.5	5.5
	110 ppm Epichlorohydrin			-
	200 ppm Propylene Oxide			61.9
2	10.2% Sodium Chloride	6	7.5	9.7
	876 ppm Propylene Glycol			11.3
	110 ppm Epichlorohydrin			90.0
	200 ppm Propylene Oxide			36.0

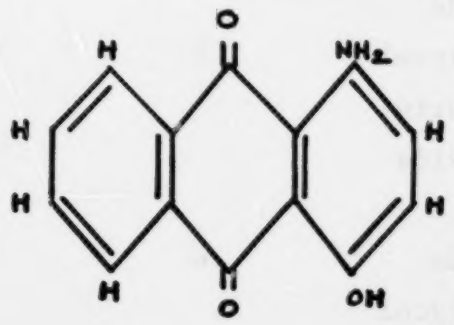
(1) Analysis performed by Dow Chemical Company, Freeport, Texas.

The chemical stability of propylene oxide and epichlorophdrin make the results questionable for these compounds.

Section VII

OTHER WASTE STREAMS

It was beyond the scope of this grant to investigate many of the industrial petrochemical waste streams for which reverse osmosis would be a potential treatment technique. In the early phases of this program, however, several solutes which represented classes of pollutants were screened to delineate areas where reverse osmosis technique would find potential applications. Of these, glycerol and polyglycols have already been discussed in this report. A disperse dye (Cibacet RED 3B) was chosen as another one of the model or representative solutes. The compound has a molecular weight of 239 and a basic structure as shown below:



This three-ring compound was selected to represent chlorinated hydrocarbons used in the production of insecticides and herbicides, unsaturated hydrocarbons such as substituted stilbenes and ethylene oxide derivatives in a reverse osmosis system. This model has a limited solubility in water and it tends to agglomerate. The results of the screening program are shown in Table 28.

In all cases excellent rejections were observed. The flux with the synthetic streams approached that of distilled water indicating little, if any, fouling of the membrane. The glycerin recovery system illustrates various problems encountered in an industrial application and each waste stream must, therefore, be evaluated for problems due to viscosity, membrane fouling and the presence of other solutes. The results indicate that this technique should be applicable to obtain excellent separations. The economics of such an operation, however, will have to be worked out for each individual system.

Further investigation of this stream was discontinued due to the lack of industrial cooperation and time.

TABLE - 28

DISPERSE ORGANIC DYE SYSTEM

MEMBRANE SOURCE : UNIVERSAL WATER CORP. (EXCEPT GSRI B-112)

MEMBRANE GEOMETRY : FLAT SHEET

SOLUTE CONCENTRATION : 1000 ppm

Membrane No.	Membrane Type	Pressure psi	Flux gfd	Rejection %
GSRI B-112	C	600	7.5	89
IV-64-2	CAB	600	61	90
		800	92.9	97.3
IV-64-2(81)	CAB	600	36.9	> 99
		800	48.4	> 99
IV-64-3	CAB	600	54.1	96
		800	58.3	97.3
IV-64-3	CAB	600	55.8	98.9
		800	62.9	> 99
IV-64-3(81)	CAB	600	22.4	> 99
		800	30.2	> 99
IV-64-4	CAB	600	36.6	94.2
		800	43.4	97.2
IV-64-4(81)	CAB	600	20.5	> 99
		800	25.4	> 99
IV-64-5	CAB	600	32.2	93
		800	34.9	94.2
IV-64-5(76)	CAB	600	47.2	> 99
		800	63.5	> 99
IV-64-5(81)	CAB	600	19.5	> 99
		800	27.5	> 99
CAB-171-15	CAB	600	7.15	> 99
		800	8.66	> 99
CAB-171-25	CAB	600	6.81	98.2
		800	9.42	> 99

Section VIII

ACKNOWLEDGMENTS

The financial support of the Louisiana State Science Foundation in the form of a grant, matching the Water Quality Office, Environmental Protection Agency grant for this project, is acknowledged with sincere thanks.

Mr. William T. Hackett, Jr., Executive Director, Louisiana State Department of Commerce and Industry, and Mr. Vernon Strickland, the Project Administrator, provided the necessary administrative assistance for the project.

Mr. Shyamkant Desai performed laboratory experiments, did calculations, evaluated the collected data and wrote an initial report. Mr. James K. Smith and Dr. Elias Klein directed project activities and helped prepare the final report. Dr. Robert E. C. Weaver of the Department of Chemical Engineering, Tulane University, New Orleans, made many valuable suggestions.

Shell Chemical Company, Norco, Louisiana, cooperated in our efforts to investigate typical industrial effluents for reverse osmosis. Mr. Robert Trautner of Shell was particularly helpful in several related discussions.

Support of the project by the Water Quality Office, Environmental Protection Agency, and the valuable suggestions provided by Mr. Lawrence Lively and Mr. James Horn, the Grant Project Officer, are acknowledged with sincere thanks.

Section IX

BIBLIOGRAPHY

1. Eller, J.R., Ford, D.L., Gloyna, E.F., *J. of AWWA*, 149 (Mar.1970).

2. Agrawal,J.R., Sourirajan, S., *Ind. Eng. Chem. Process Des. Develop.*, 9, No. 1 (January 1970).

3. Kimura, S., Sourirajan, S., *A.I.Ch.E.J.*, 13 497(1967).

4. Desai, S.V., M.S. Thesis, Department of Chemical Engineering, Tulane University, New Orleans.

5. Shreeve, N., *Chemical Process Industries*, McGraw Hill Publications, 564, ed. 1968.

6. American Standard Product Information Manual for the Pilot Unit.

7. Office of Saline Water, Research and Development Progress Reports, Nos. 143, 339.

8. Brian, P.L.T., *Ind. Eng. Chem. Fundam.*, 4, 439(1965).

9. Dresner, L., *J. Phys. Chem.*, 69, 2230(1965).

10. Tien, C. and Gill, W.N., *A.I.Ch.E.J.*, 12, 722(1966).

11. Peters, M., *Plant Design and Economics for Chemical Engineers*, McGraw Hill Publications, New York, 1958.

12. Perry, J.H., *Chemical Engineers' Handbook*, McGraw Hill Publications, New York, 4th edition, Section 26.

Section X

APPENDIX

CHEMICAL ANALYSIS OF GLYCERIN WASTE STREAM

Glycerin Determination:

A 3 ml sample was added to a small beaker along with 25 ml deionized water. The pH was adjusted to 6 using 0.5N HCl. The contents of the beaker were then poured through a 50 ml buret filled with 30 ml of Amberlite IRA-400 resin in the chloride form. The resin was washed with 100 ml deionized water. The sample and all washings were collected in a large Erlenmeyer flask. The pH of this sample was brought to between 3 and 4 using 0.5N HCl. One drop of Dow Corning Antifoam B was added and nitrogen was bubbled through the sample for 15 minutes. Then 3 drops of 0.5% methyl red indicator was added and the sample was neutralized with 0.1N NaOH. 50 ml of 5% sodium periodate was added, the flask was stoppered and allowed to stand for 10 minutes. Next, 5 ml of 50%v ethylene glycol was added and the flask was allowed to stand for 5 minutes. Three drops of methyl red indicator were added and the solution was titrated with 0.1N NaOH to the end point.

A blank was run for each batch of sodium periodate used.

Note: All compositions referred to in this section are percent by weight unless otherwise mentioned.

Calculation:

$$\% \text{ Glycerin} = \frac{(A)(B)(9.21)}{(C)(D)}$$

where,

A = Volume of 0.1N NaOH required to reach end-point, minus the blank.
B = Normality of NaOH used.
C = Volume of the original sample used.
D = Specific gravity of the original sample, by hydrometer (range: 0.9 - 1.2).

Water Determination:

Duplicate samples, approximately 5 grams each, were weighed on a Mettler balance in previously tared porcelain crucibles. The crucibles were then placed in an oven at a temperature of 110°c for a minimum of 4 hours. The samples were then removed from the oven and placed in a desiccator for 1 hour. The samples were reweighed.

Calculation:

$$\% \text{ Water} = \frac{(Z - Y)}{(X - Y)} \times 100$$

where,

X = Weight of the crucible plus the weight of the original sample.
Y = Tare weight of the porcelain crucible.
Z = Weight of the crucible plus the weight of the sample after being heated to 110°c for 4 hours.

Inorganic Determination:

The samples used for water determination were then placed in a muffle furnace at 700°c for 4 hours. The crucibles were allowed to cool considerably in the muffle furnace before being placed in a desiccator for 1 hour. The samples were then weighed.

Calculation:

$$\% \text{ Inorganics} = \frac{(S - R)}{(Q - R)} \times 100$$

where,

Q = Weight of the crucible plus the weight of the original sample used in the water determination.
R = Tare weight of the crucible.
S = Weight of the crucible plus the weight of residue after ignition in the muffle furnace

Polyglycerine Determination:

Knowing the percent by weight composition of the other three components in the system, the percent by weight composition of polyglycerines was found by difference.

Calculation:

$$\% \text{ Polyglycerines} = 100 - (G + W + I)$$

where,

G = % Glycerin.
W = % Water.
I = % Inorganics.

Table 29 illustrates the typical reproducibility of the analysis duplicate samples analyzed concurrently. Variations in day-to-day operations lead to the larger deviation quoted on page 13.

TABLE - 29

REPRODUCIBILITY OF ANALYTICAL RESULTS

Sample #	% H_2O By Weight Loss	% H_2O Karl Fisher	% Inorganic	% Organic
DS 24 F	86.94	87.35	1.77	11.29
	86.73		1.78	11.49
FS 24 P	98.17	96.85	.10	1.73
	98.24		.10	1.66
RE 5 F	88.97	86.45	1.48	9.55
	89.04		1.49	9.47
RE 5 P	97.79	98.95	.08	2.13
	97.80		.08	2.12

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM

5 Organization

GULF SOUTH RESEARCH INSTITUTE, New Orleans, Louisiana.

6 Title

POLYMERIC MATERIALS FOR TREATMENT AND RECOVERY OF PETROCHEMICAL WASTES

10 Author(s)

Klein, Elias
Desai, Shyamkant V.
Smith, James K.
Weaver, Robert E. C.

16 Project Designation

EPA Grant No. 12020DQC

21 Note

22 Citation

Final Report, October 1970, Water Quality Office, Environmental Protection Agency. 68 pages, 12 figures, 29 tables, 12 references.

23 Descriptors (Starred First)

*Reverse Osmosis, *Membranes, *Separation-Techniques, *Water Pollution Treatment, Effluents, Neutralization, Viscosity, Pressure, Economic Evaluation.

25 Identifiers (Starred First)

Flux, Rejection, Recovery, Concentration, Multistage Operation.

27 Abstract

Reverse osmosis is used as a unit operation to study the utility of polymeric membrane materials for petrochemical plant waste treatment. A glycerin plant waste stream containing glycerin, polyglycerines and inorganics was treated using cellulose acetate butyrate memoranes. These membranes offered best performance in the pressure range 600-800 psig. The data, obtained on a semi-pilot scale equipment, was used to project a plant scale operation. It is shown that such a recovery is possible, using single or multistage designs with an attractive return on investment. The report also includes preliminary studies on disperse dye and propylene glycol plant waste stream. (SVD).

Abstractor	Institution

WR:102 (REV. JULY 1969)
WRSIC

SEND TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

* GPO: 1969—359-339